188. *The Application of Infrared Spectroscopy to a Study of Some Reaction Intermediates and Products of the Autoxidation of Long-chain Olefins.**

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The action of gaseous oxygen on methyl oleate and elaidate, long-chain α-diols, epoxides, α-ketols, and α-diketones has been examined. No " elaidinisation " of methyl oleate occurs during autoxidation, suggesting that *trans*-hydroperoxides are formed from both methyl oleate and elaidate. α-Diols and *cis*- and *trans*-epoxides are not oxidised, but α-ketols and α-diketones are, forming smaller acids by way of hydroperoxides, α-diketones being intermediates in the oxidation of α-ketols. α-Diols and α-ketols are polyesterified in the presence of free carboxylic acid. The configurations of the epoxide (*cis* and *trans*) and α-diol (*threo* and *erythro*) products of olefin autoxidation are related to the geometrical isomerism of the initial olefin. A general scheme of olefin autoxidation is outlined.

In recent years the autoxidation products of several olefinic compounds have been isolated. These consist mainly of α-diols, epoxides, scission acids, and minor amounts of α-ketols.[1] Less attention has been paid to the mode of formation of these products from olefins, their interaction, their behaviour on further oxidation to ascertain whether they are intermediates or end-products, and their configuration in relation to that of the olefinic starting material. Some of these problems have now been attacked and the results allow a statement of the broad features of a general reaction scheme for the complex autoxidation of olefins. The compounds specifically investigated were methyl oleate and elaidate; α-ketols, α-diketones, *cis*- and *trans*-epoxides, and *threo*- and *erythro*-diols derived

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* For a preliminary account, see *Research*, 1956, **9**, 519.

[1] (*a*) Skellon, *J. Soc. Chem. Ind.*, 1931, **50**, 382T; (*b*) Ellis, *Biochem. J.*, 1950, **46**, 129; (*c*) Feuell and Skellon, *J.*, 1954, 3414.

from octadecenoic acids; as well as lauroin and the corresponding diketone, tetracontane-12 : 13-dione.

EXPERIMENTAL

Autoxidations were carried out in the presence of uranium petroselinate (0·2% by wt.) at 120°, unless stated otherwise. Samples were withdrawn and analysed chemically [2] and spectroscopically. The infrared spectra of liquids were determined as films, and those of solids as Nujol mulls.

Autoxidation of Methyl Oleate (*Octadec*-cis-9-*enoate*) *and Elaidate* (*Octadec*-trans-9-*enoate*).—*Infrared spectroscopic analysis.* Infrared absorption spectra were taken on a Grubb-Parsons double-beam instrument on thin films of the oils by themselves, in a cell with adjustable path-length. For short path-lengths an internal standard, *viz.*, the band at 3·46 μ (for methyl elaidate) or 3·48 μ (for methyl oleate), which is due to C–H stretching vibrations, was used, the concentration c of any particular group present during the oxidation being given by c = Constant × D_a/D_b, where D_a = optical density at which the group absorbs, and D_b = optical density at the wavelength of the " standard " band. This relation was used in the analysis of unsaturation and of carboxyl and hydroxyl groups. For thicker films the use of an internal standard was unnecessary. Where checked, both methods gave identical results, except at the highest absorption intensities.

Autoxidation of esters. Methyl oleate (b. p. 168—170°/2 mm.; from oleic acid purified by low-temperature crystallisation from acetone) or methyl elaidate (b. p. 199—200°/8·5 mm.) was oxidised in a wide tube with a deep ground-glass joint, the stopper of which was equipped with an inlet delivery tube tapered to a fine nozzle, outlet, stirrer guide, and apertures for a thermometer and for removal of samples. Oxygen, dried by concentrated sulphuric acid, was admitted at a rate of 50 ml. per min., and stirring was at approx. 200 r.p.m. The results are in Tables 1 and 2, to which the following notes apply.

(*a*) Obtained from 100 × ratio of [Constant × $D_{10.32}/D_{3.46}$ (for methyl elaidate)] to the theoretical initial oidine value, where the constant = 85·61 ÷ $D_{10.32}/D_{3.46}$ (initial).

(*b*) Given by 100 × ($D_{3.18}/D_{3.46}$) less initial value.

(*c*) Calculated from the actual acid value and the theoretical maximum acid value (on the assumption that all the methyl elaidate is quantitatively converted into scission acids, $CH_3{\cdot}[CH_2]_n{\cdot}CO_2H$ and $CO_2H{\cdot}[CH_2]_{13-n}{\cdot}CO_2Me$ and CO_2).

(*d*) Given by 100 ($D_{6.1}/D_{3.46}$) less the initial value. After 390 min. accurate measurement was impossible, because of the general increase in intensity at 5—6 μ.

(*e*) Calculated from the actual active-O % and oxiran-O % and the theoretical values (4·87, 5·119) for the hydroperoxide and epoxide, respectively.

(*f*) *I.e.*, sap. val. − (acid val. + initial sap. val.).

TABLE 1. *Autoxidation of methyl elaidate* (25 *g.*).*

Time (min.)	0	12	35	72	130	210	285	290	390	450	515	575
Unsaturation (%)												
Spectroscopic [a]	100	—	98	98	86	57	31	—	15	7	5	4
Chemical	100	99	100	97	—	67	46	—	27	17	11	8
Intensity of band at 3·18 μ [b]	0·0	—	0·4	0·6	1·0	4·0	8·0	—	12·3	15·1	17·5	19·3
Carboxyl (%) (chemical) [c]	0·0	—	—	—	1·5	5·8	—	—	18·0	20·5	—	25·1
Intensity of band at 6·1 μ [d]	0·0	—	0·0	0·0	1·7	4·9	7·0	—	6·4	—	—	—
Hydroperoxide (%) [e]	0·0	—	—	5·3	16·3	17·8	11·4	—	6·3	5·2	—	4·2
Epoxide (%) [e]	0·0	—	—	—	5·7	—	—	11·0	—	9·4	—	5·3
α-Diol (%)	0·0	—	—	0·0	—	6·1	—	—	10·6	—	—	12·0
Sap. val.	189	—	—	190	—	—	236	—	—	286	315	336
Additional ester [f]	0	—	—	1	—	—	11	—	—	31	52	66

* For notes see main text.

Spectroscopic analysis of carbonyl groups. Both methyl elaidate and oleate show [3] single carbonyl bands at 5·75 μ. In both cases bands, at 5·81, 5·85, 6·1, and later at 5·6 μ appeared

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[2] Analyses: peroxide, Skellon and Wills, *Analyst*, 1948, **73**, 78; epoxide, Swern, Findley, Billen, and Scanlan, *Analyt. Chem.*, 1947, **19**, 414; hydroxyl, Ogg, Porter, and Willits, *Ind. Eng. Chem. Anal.* 1945, **17**, 394; other analyses, Knight and Swern, *J. Amer. Oil Chemists' Soc.*, 1949, **26**, 366.

[3] Shreve, Heether, Knight, and Swern, *Analyt. Chem.*, 1950, **22**, 1498.

TABLE 2. *Autoxidation of methyl oleate* (25 *g.*).*

Time (min.)	0	50	60	100	125	187	220	340	460	490	570	580
Unsaturation (%)												
Chemical	100	—	—	75	67	—	43	27	20	—	—	—
Intensity of band at 3·18 μ [b]	0·0	0·0	—	—	2·5	4·5	—	8·5	—	11·7	13·3	—
Carboxyl (%) [c]	0·0	—	—	—	2·7	4·3	—	9·5	—	15·0	18·7	—
Hydroperoxide (%) [e]	0·0	—	11·7	21·4	—	—	19·3	12·7	6·4	—	—	4·1
Epoxide (%) [e]	0·0	—	—	—	6·5	—	—	11·3	—	—	—	5·1
α-Diol (%)	0·0	0·0	—	—	—	—	6·0	—	—	—	—	10·5
Sap. val.	189	—	—	—	210	—	229	—	—	318	351	—
Additional ester [f]	0	—	—	—	12	—	22	—	—	80	102	—

* For notes see main text.

and increased in intensity as the oxidation proceeded. The following products were separated from the autoxidation residue from methyl elaidate (oxidised for 575 min. at 120°): (1) Free acidic products separated by alkaline extraction followed by acidification [bands at 5·70 (sh = shoulder), 5·75(sh), 5·80, 5·85, 5·91 μ]. (2) Neutral products remaining after products (1) had been removed [bands at 5·6 (broad sh), 5·75, 5·81, 5·84(sh), 6·1(sh) μ]. These neutral products were hydrolysed, and the acids (3) separated [bands at 5·76, 5·80, 5·86, 5·92 μ similar to those of (1)]. After removal of the acids (3) from material (2), the product gave bands at 5·6(small sh) and 5·75 μ. Therefore the bands at 5·81 and 5·85 μ must be due, at least in part, to acidic products.

Autoxidised methyl elaidate (at 120°) shows a band at 6·1 μ [also apparent in material (2), above]. This could be due to *cis*-ethylenic compounds[4] or αβ-unsaturated ketones.[5] The band is assigned to the latter, since the band is more intense than that in *pure* methyl oleate and occurs at a longer wavelength. Also, the intensity of the band is greater in methyl elaidate autoxidised for 20 hr. at 85° [hydroperoxide 28·5%: unsaturation (iodometric) 42% and (spectroscopic) 38%] and αβ-unsaturated ketones are known to be formed in greater amount at this lower temperature.[1b] The band at 5·6 μ may possibly be due to saturated lactones, since it is almost completely removed by hydrolysis.

Autoxidation of α-Ketols.—Autoxidation of 6 : 7- and 7 : 6-hydroxyoxostearic acids led to oils of high molecular weight, as a result of some polyesterification, and separation of the products appeared unpromising from preliminary experiments.

Autoxidation of lauroin. Lauroin (3·8 g.), m. p. 61° (prepared by Hansley's method [6]), was oxidised for 8·5 hr. Volatile products were collected at −78°. Carbon dioxide evolved was estimated by reaction with barium hydroxide. Carbonyl analysis fell continuously and a maximum peroxide value of 0·03 (active O%) was obtained after 165 min.

The residue (2 g.; acid value, 150) after the oxidation was dissolved in ether and treated with sodium carbonate solution, and the two layers were separated.

The neutral ethereal extracts were washed with aqueous sodium carbonate, then water, and dried (Na_2SO_4). After removal of the ether, the cooled residue gave, on fractional crystallisation from ethanol, pale yellow crystals (0·2 g.), m. p. 70° (mixed m. p. with tetracontane-12 : 13-dione, 71°) and a more soluble cream-coloured solid (0·4 g.), m. p. 58° (mixed m. p. with lauroin, 61°). The alkaline aqueous layer was acidified and extracted with ether. The extracts were dried (Na_2SO_4), the ether was evaporated, and the residue (1·1 g.) crystallised from ethanol to m. p. 37°. The m. p. of the *p*-bromophenacyl derivative was 72° alone or mixed with that of dodecanoic acid, but was depressed to 64—65° on admixture with that of undecanoic acid (m. p. 68°). The condensed volatile matter consisted of traces of water and an immiscible colourless liquid (0·1 g.). This gave a pink colour with Schiff's reagent, indicating the presence of an aldehyde, and an infrared spectrum identical with that of lauric acid, presumably formed by oxidation of the aldehyde. The 2 : 4-dinitrophenylhydrazone (m. p. 103°) gave no m. p. depression on admixture of that of undecanal (m. p. 104°).

6 : 7-*Dioxostearic Acid.*—The mixed 6 : 7- and 7 : 6-hydroxyoxostearic acids (5 g.) were added to chromic acid (3 g.) in glacial acetic acid (300 ml.) with shaking. After 36 hr. at room temperature the solution was diluted with water (300 ml.). The solid precipitate was filtered off and recrystallised from ethanol as pale yellow crystals, m. p. 97° (2·3 g., 46%) (Found: C, 69·0;

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[4] McCutcheon, Crawford, and Welsh, *Oil and Soap*, 1941, **18**, 9.

[5] Sinclair, McKay, Myers, and Jones, *J. Amer. Chem. Soc.*, 1952, **74**, 2578.

[6] Hansley, *J. Amer. Chem. Soc.*, 1935, **57**, 2303.

H, 10·1. Calc. for $C_{18}H_{32}O_4$: C, 69·2; H, 10·3%). Steger and van Loon [7] report m. p. 98° for 6 : 7-dioxostearic acid, prepared by potassium permanganate oxidation of octadec-6-ynoic acid.

Methyl 9 : 10-*Dioxostearate*.—Methyl *threo*-9 : 10-dihydroxystearate (5 g.) was oxidised by the same method to give, on recrystallisation from ethanol, pale yellow *methyl* 9 : 10-*dioxostearate*, m. p. 50° (2·9 g., 58%) (Found: C, 69·8; H, 10·3. $C_{19}H_{34}O_4$ requires C, 69·9; H, 10·5%).

Methyl 6 : 7-*Dioxostearate*.—Methyl *threo*-6 : 7-dihydroxystearate (1 g.) was oxidised as above to give, on recrystallisation from ethanol, pale yellow *methyl* 6 : 7-*dioxostearate*, m. p. 61° (0·5 g., 51%) (Found: C, 69·75; H, 10·3%).

Tetracontane-12 : 13-*dione*.—This diketone, m. p. 71° (5 g., 50%), was prepared as above from lauroin (10 g.). Hansley [6] reports m. p. 71·0—71·5° for the same compound, prepared by oxidation of lauroin with Wijs's solution.

Autoxidation of α-Diketones.—6 : 7-*Dioxostearic acid*. After 475 minutes' oxidation the infrared spectrum (liquid film) is similar to, and contains all, the absorption bands of adipic acid and additional bands at 8·07, 7·77, and 9·24 μ. These are present in the spectrum of lauric acid. After 475 min. the acid value (initial 177) and saponification value were 305 and 418 respectively.

Autoxidation of tetracontane-12 : 13-*dione*. The results were :

Time of oxidation (min.)	0	100	240	300	525	575
Peroxide [active O (%)]	0·00	0·30	0·27	0·14	0·00	—
Carbonyl (%)	15·3 *	—	—	9·0	—	—
Unsaturation (I value)	—	5·1	6·0	—	—	—
CO_2 (g.) (from 5·3 g. of diketone)	—	—	—	—	—	0·13

* Theor. initial value, 15·3.

The residue (2·0 g.; acid value, 157) from the oxidation of 5·3 g. of diketone for 575 min. was dissolved in ether and extracted with sodium carbonate solution. The alkaline layer was separated and acidified, the liberated acids were extracted with ether, and the extracts dried (Na_2SO_4). After evaporation of the ether, the residue was cooled and recrystallised from ethanol to m. p. 39° (1·2 g.). The compound was identical (mixed m. p. and infrared spectrum) with lauric acid. Its *p*-bromophenacyl derivative had m. p. 72° alone or mixed with that of lauric acid.

The neutral ethereal extract was dried (Na_2SO_4) and the ether evaporated. The semisolid residue (two of its infrared absorption bands were at 2·90 and 6·11 μ) gave some tetracontane-12 : 13-dione (0·05 g.; identified by mixed m. p.) on attempted crystallisation from ethanol. Evaporation of the ethanolic mother-liquor gave a semisolid residue (0·3 g.) which was not identified. The volatile matter collected in the trap consisted of traces of water and an aldehyde (0·3 g.) identified as previously as undecanal.

Autoxidation of methyl 9 : 10-*dioxostearate*. The results were:

Time of oxidation (min.)	0	50	110	205	345
Peroxide [active O (%)]	0·00	0·00	0·15	0·05	0·00
CO_2 (g.) (from 3 g.)	—	—	—	—	0·11

The residue (1·2 g.), from the oxidation of methyl 9 : 10-dioxostearate (3 g.) for 6 hr., was dissolved in ether and extracted with aqueous sodium carbonate. The alkaline extract was acidified and steam-distilled. Solid zinc sulphate was added to the neutralised distillate, and the solid precipitate was filtered off, recrystallised from ethanol, and identified as zinc nonoate (m. p. 133° alone or mixed with zinc nonoate). The cooled residue from the distillation was hydrolysed, acidified, and extracted with ether. These extracts were dried (Na_2SO_4) and the solvent evaporated. The residual azelaic acid, on crystallisation from water, had m. p. 107° (mixed m. p. and infrared spectrum).

The neutral ethereal extract was dried, and the solvent evaporated. A liquid film of the cooled residue gave a spectrum including, amongst others, bands at 2·90 and 6·11 μ. No methyl 9 : 10-dioxostearate was recovered. A spectrum of the condensed volatile matter gave absorption maxima corresponding to those of a mixture of azelaic acid and water.

Effect of Heat and Gaseous Oxygen on Epoxides and Diols.—*Methyl* trans-9 : 10-*epoxystearate*. When the ester (m. p. 32°; 5·5 g., prepared from methyl elaidate by oxidation with perbenzoic acid [8]) was treated with gaseous oxygen, analyses for oxiran-oxygen and peroxide indicated

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[7] Steger and van Loon, *Rec. Trav. chim.*, 1933, **52**, 593.

[8] Swern, " Organic Reactions," John Wiley and Sons, New York, 1953, Vol. VII, p. 396.

that no oxidation had occurred. The spectra were all identical with the spectrum of the pure *trans*-epoxide (identical with that published [9] for the same compound).

The infrared spectrum was unchanged when the *trans*-epoxide (0·5 g.) was heated in a sealed tube at 120° for 7 hr.

Methyl cis-6 : 7-*epoxystearate.* The above experiment was repeated with methyl *cis*-6 : 7-epoxystearate, m. p. 27° (prepared from methyl petroselinate by oxidation with perbenzoic acid). The infrared spectra of the *cis*-epoxide before and after attempted oxidation for 7 hr., and after 7 hours' heating alone were identical. The spectra of the *cis*- and *trans*-epoxides were determined in all cases as liquid films. The epoxides in the solid or partially crystalline state give more detailed spectra and have bands at slightly different wavelengths.

erythro-6 : 7-*Dihydroxystearic acid* (m. p. 121°; 18 g.). The molten acid (prepared from petroselinic acid by oxidation with alkaline potassium permanganate) was oxidised for 540 min. at 123°:

Time (min.)	0	150	270	420	540
Carboxyl (%)	93·1	77·3	74·4	70·9	69·7
Hydroxyl (%)	—	83·6	73·0	59·1	49·0

The pale yellow product (2·0 g.; m. p. 92—93°; mean *M*, 450; initial *M*, 317; sap. val., 273; ester val., 149; carbonyl %, 0·0; oxiran-O %, 0·0) was hydrolysed, then treated with chloroform–light petroleum to extract any hydroxyoxo-acids present. Only unchanged *erythro*-6 : 7-dihydroxystearic acid (1·3 g.) was recovered, in addition to a trace of oil with a sweet ester odour.

threo-9 : 10-*Dihydroxystearic acid.* The acid (m. p. 95°; 18 g.) (prepared both from oleic and from elaidic acid by oxidation with formic acid and hydrogen peroxide,[8] and aqueous alkaline potassium permanganate, respectively) was oxidised for 500 min.:

Time (min.)	0	130	310	440
Carboxyl (%)	96·8	92·5	89·7	88·7
Hydroxyl (%)	95	—	53	43

The product had *M*, 440 (initial *M*, 317), m. p. 71·5—73°, oxiran-O %, 0·0.

Methyl threo-9 : 10-*dihydroxystearate.* The ester, m. p. 93°, was prepared from methyl oleate, acetic acid, and hydrogen peroxide by adaptation of Dorée and Pepper's method[10] for methyl 13 : 14-dihydroxybehenate. Analyses for hydroxyl, ester, carbonyl, and epoxide groups during treatment with gaseous oxygen for 600 min. indicated absence of oxidation. However, when the above ester was heated with azelaic acid in a closed vessel for 415 min. at 120°, the acid and hydroxyl values fell from 280 and 186 to 248 and 146, respectively. Under the same conditions, no reaction occurred between the ester and methyl *trans*-9 : 10-epoxystearate.

Isolation of Dihydroxy-acid from Autoxidised Methyl Elaidate.—A procedure similar to that used by King [11] was employed. The isolated dihydroxystearic acid, m. p. 129—130°, gave an infrared spectrum which was identical with that of pure *erythro*-9 : 10-dihydroxystearic acid.

Isolation of Dihydroxy-acids from Autoxidised Methyl Oleate.—The accurately weighed product (*ca.* 2 g.) from the autoxidation of methyl oleate at 120° was hydrolysed, diluted with water, acidified, and cooled. The mixture was then extracted with ether, the ethereal extracts were dried (Na_2SO_4), and the solvent was evaporated. Light petroleum (b. p. 40—60°; 100 ml.) was added to the residue, and the mixture stirred and cooled in the refrigerator overnight. The white solid precipitate, m. p. 100—105°, was filtered off through a weighed sintered-glass crucible, washed with light petroleum, dried, and weighed. Its infrared spectrum showed the compound to be a mixture of *erythro*- with some *threo*-9 : 10-dihydroxystearic acid. A spectrum of the same mixture, after recrystallisation from ethanol, showed that the proportion of the *threo*-form had increased.

DISCUSSION

Scheme of Olefin Autoxidation.—A study of the intensity of the band at 10·32 μ (associated with a *trans*-double bond [12]) during the autoxidation of methyl elaidate shows that the double bond is scarcely attacked in the initial stages when the hydroperoxide

[9] Shreve, Heether, Knight, and Swern, *Analyt. Chem.*, 1951, **23**, 277.
[10] Dorée and Pepper, *J.*, 1942, 477.
[11] King, *J.*, 1954, 2114.
[12] Bellamy, " The Infra-Red Spectra of Complex Molecules," Methuen and Co., London, 1954.

concentration [as shown by chemical analysis (Table 1) and the intensity of the band at 2·9 μ[13]] is increasing, and that the most rapid decrease in unsaturation occurs simultaneously with hydroperoxide decomposition and the onset of secondary reactions. These analyses support the view that the formation of an unsaturated hydroperoxide[14] is the initial stage of olefin autoxidation. [In addition the spectroscopic analysis for unsaturation allows a comparison with Wijs's method based on iodine absorption (Table 1). Discrepancies may be due to the unreliability of the latter in the presence of peroxide.[15]] Moreover the fact that 2 : 2 : 5 : 5-tetramethylhex-3-ene and 1 : 2-diphenylethylene (both lacking α-methylenic groups) will not undergo autoxidation in the absence of a hydroperoxide[16] suggests that initiation occurs at the α-methylenic group[14] (cf. ref. 17).

No evidence for the formation of *cis*-olefin during the autoxidation of methyl elaidate was obtained, from examination of either the absorption near 6 μ or the region about 13·8 μ. These observations accord with the fact that no traces either of *cis*-epoxide[18] or of *threo*-9 : 10-dihydroxystearic acid were isolated from the autoxidation products of methyl elaidate. It is therefore concluded that methyl elaidate does not isomerise to methyl oleate during the oxidation. Since the *cis*–*trans* equilibrium[19] in the elaidinisation of oleic acid is 1 : 2, production of *cis*-isomer would be expected to be in recognisable amount if the two isomers were in equilibrium during the autoxidation. Knight, Eddy, and Swern[20] observed the growth of the band at 10·32 μ during the autoxidation of methyl oleate at 35°, and showed that the concentration of *trans*-material corresponded to approx. 90% of the concentration of hydroperoxide formed. Their five suggestions for the mode of formation of *trans*-unsaturation can be reduced to two main issues: either there is isomerisation of methyl oleate to methyl elaidate during the oxidation, or methyl oleate gives rise to *trans*-unsaturated hydroperoxides. They argued that in the latter case, *two trans*-hydroperoxides (methyl 9-hydroperoxyoctadec-*trans*-10-enoate and 10-hydroperoxyoctadec-*trans*-8-enoate) would be formed from methyl oleate. The observation quoted above, *viz.*, the failure of methyl elaidate to isomerise to methyl oleate, suggests that methyl oleate would also not be isomerised to any extent to methyl elaidate. Thus the present work supports the second alternative, that methyl oleate forms *trans*-unsaturated hydroperoxides. However, there is strong experimental evidence[21] that *four* (not only *two* in the case of methyl oleate; cf. ref. 20) hydroperoxides would be formed from either methyl oleate or elaidate. The formation of *four trans*-hydroperoxides can be reasonably explained (cf. ref. 20) on the assumption that the mesomeric radical, formed by abstraction of an α-methylenic hydrogen atom, does not retain configuration about the site of the initial double bond, and that *trans*-configurations about the two partial double bonds in the radical are preferred.

The results in Table 1 shows that the intensity of the band at 6·1 μ (a measure of the concentration of αβ-unsaturated ketones) reaches a maximum after the maximum concentration of hydroperoxide has been passed, *i.e.*, the formation of unsaturated ketones occurs at a later stage and therefore these are not precursors of the hydroperoxides but are formed from them.[22] The concentration of these unsaturated ketones decreases as they are further oxidised.[23] Chemical analyses, during autoxidation of methyl oleate or elaidate, show that after the growth of hydroperoxide and during its decomposition the

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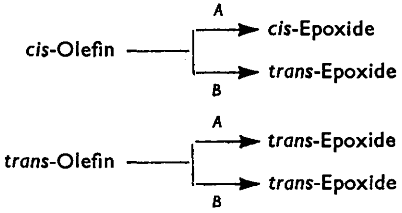
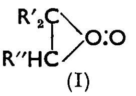
[13] Shreve, Heether, Knight, and Swern, *Analyt. Chem.*, 1951, **23**, 282.
[14] Farmer, *Trans. Faraday Soc.*, 1942, **38**, 340, 356; Farmer and Sutton, *J.*, 1943, 119, 122.
[15] Knight, Coleman, and Swern, *J. Amer. Oil Chemists' Soc.*, 1951, **28**, 498.
[16] Hawkins and Quin, *J. Appl. Chem.*, 1956, **6**, 1.
[17] Hilditch, *J. Oil Colour Chemists' Assoc.*, 1947, **30**, 1.
[18] Ellis, *Biochem. J.*, 1936, **30**, 753.
[19] Griffiths and Hilditch, *J.*, 1932, 2315.
[20] Knight, Eddy, and Swern, *J. Amer. Oil Chemists' Soc.*, 1951, **27**, 188.
[21] Ross, Gebhart, and Gerecht, *J. Amer. Chem. Soc.*, 1949, **71**, 282; Bickford, Fisher, Kyame, and Swift, *J. Amer. Oil Chemists' Soc.*, 1948, **25**, 254; Swift, Brown, and O'Connor, *ibid.*, p. 39.
[22] Cf. Ellis, *J.*, 1950, 9.
[23] Hawkins, *J.*, 1955, 3288.

production of epoxide and acid occurs, followed in turn by hydroxyl groups. The epoxide concentration reaches a maximum and then decreases, whereas hydroxyl and acid concentrations continue to increase. The appearance and increase of acid can alternatively be shown by the intensity of the band at 3·18 μ, which provides a semiquantitative analysis, or by the bands at 5·81 and 5·85 μ. The acids, and in addition carbon dioxide, result from the further autoxidation of hydroperoxides.[24]

The method of formation of epoxides in the autoxidation of olefins is unknown. However, it is known that *cis*-olefins give a mixture of *cis*- and *trans*-epoxides, whereas *trans*-olefins give only *trans*-epoxides.[18] Isolated hydroperoxide, heated with a *cis*-olefin, gives an epoxide,[25] the reported properties of which indicate epoxidation by *cis*-addition to the double bond. As it was found that *cis*- and *trans*-epoxides do not isomerise under the conditions of an autoxidation and that the parent olefins do not undergo elaidinisation, it appears that the *trans*- and *cis*-epoxides are formed from *cis*-olefins by *two* concurrent reactions, *viz.*, (*A*) *cis*-epoxidation (by oxidation by the hydroperoxide molecule) and (*B*) a non-stereospecific two-step reaction. Route (*B*) involves in its first step the addition of a radical (such as $\cdot O_2H$ or $\cdot O_2R$) at one end of the double bond, giving a free radical in which rotation about the position of the original double bond can occur. In the second step, the epoxide ring is closed, after or simultaneously with rupture of the peroxide link in the radical. To explain the stereochemical result, this second step would have to yield exclusively the "*trans*"-compound (which is presumed to be the more stable isomer). The different stereochemical results for epoxide formation during the autoxidation of *cis*- and *trans*-olefins can thus be accommodated:



This dual mechanism would help to explain the high yields of epoxides [26] which can be obtained in the presence of alkali, under conditions where the amounts of hydroperoxide are too low to be compatible with the occurrence of epoxidation by direct attack of hydroperoxide. By route (*B*) only a small amount of hydroperoxide would suffice to initiate a chain reaction leading to extensive epoxide formation. Gasson, Millidge, Primavesi, Webster, and Young [26] explained this result by postulating that epoxidation proceeds by way of a moloxide [27] (I) but it is not apparent why this mode of reaction should not lead exclusively to *cis*-epoxidation. The eventual decrease in epoxide concentration, during olefin autoxidation, must be due to their ring-opening by water and acids [28] (present in the autoxidation products) to form free α-diol or its monoacyl derivative, since it was found that methyl *trans*-9 : 10- and *cis*-6 : 7-epoxystearate are both unaffected by gaseous oxygen at 120° in the presence of a uranium soap catalyst (cf. ref. 27). There was likewise no change if the epoxide esters were heated to that temperature by themselves or with an α-diol.



(I)

The infrared spectra of the pure *threo*- and *erythro*-isomers of both 9 : 10- and 6 : 7-dihydroxystearic acid were clearly distinguishable. The crude 9 : 10-dihydroxystearic acid, isolated from the autoxidation of methyl elaidate at 120°, gave a spectrum identical with that of pure *erythro*-9 : 10-dihydroxystearic acid, whilst the crude dihydroxy-acid, from the same reaction of methyl oleate, gave one showing it to be a mixture of *erythro*- with some

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[24] Atherton and Hilditch, *J.*, 1944, 105.

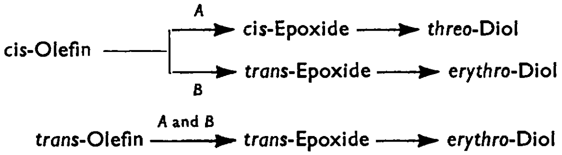
[25] Swift and Dollear, *J. Amer. Oil Chemists' Soc.*, 1948, **25**, 52.

[26] Gasson, Millidge, Primavesi, Webster, and Young, *J.*, 1954, 2161.

[27] Paquot, *Bull. Soc. chim. France*, 1945, **12**, 120.

[28] Nicolet and Poulter, *J. Amer. Chem. Soc.*, 1930, **52**, 1186.

threo-isomer, *i.e.*, *cis*-olefin produces a mixture of *threo*- and *erythro*-diol, and a *trans*-olefin produces an *erythro*-diol only. Since long-chain epoxides undergo ring-opening with complete inversion[29] *cis*- and *trans*-epoxides would be the precursors of *threo*- and *erythro*-diols respectively. Thus the stereochemistry of the diols can be linked with the configurations of the epoxide products of the olefin autoxidations:



Methyl *threo*-9 : 10-dihydroxystearate was unchanged when heated alone or under the usual conditions of the autoxidation experiments. However, esterification occurred in the presence of compounds containing free carboxyl groups. Similarly, no oxidation took place when *threo*-9 : 10- or *erythro*-6 : 7-dihydroxystearic acid was treated with gaseous oxygen, the only changes being extensive intermolecular (and possibly some intramolecular) esterification: no epoxides or α-ketols were formed. The above accounts for the relatively large amounts of α-diols (approx. 10—15%) isolated, after hydrolysis, from the olefin-autoxidation product, and the high " additional ester " values obtained (66—102, *i.e.*, 2—3 times greater than can be explained on the assumption that the alkali is all used in hydrolysing monoacyl derivatives of dihydroxystearic acid).

The method of formation of α-ketols is unknown, though it has been shown that they are not obtained on autoxidation of α-diols. The α-ketol products undergo autoxidation themselves (which accounts for their low concentration in the end-products of olefin oxidation[1c]), the first isolable product being the α-diketone which is then itself oxidised to the scission acids. Thus, after reaction for 8·5 hr. at 120°, the following products were isolated from the autoxidation of lauroin (numbers refer to parts by wt. of product per 100 parts of lauroin): tetracontane-12 : 13-dione, 10; dodecanoic acid, 55; undecanal, 2·6; carbon dioxide, 0·7; lauroin (recovered), 20; water, a trace. The intermediate formation of the diketone could be followed in the infrared spectra of samples of the reaction mixture. These showed a continuous decrease of the alcoholic OH-stretching band at 3·0 μ, and the growth to a maximum intensity and then decrease of bands at 5·82, 10·85, and 13·79 μ. The last bands are characteristic of the spectrum of pure tetracontane-12 : 13-dione. They disappear entirely on prolonged oxidation, the spectrum becoming similar to that of pure lauric acid.

An analogous study of the autoxidation of a mixture of 6 : 7- and 7 : 6-hydroxyoxostearic acid was complicated by the formation of oils of high molecular weight as a result of polyesterification, indicating the ready esterification of α-ketols.

Since the above experiments showed the intermediate formation of α-diketones, autoxidation of some of these compounds was investigated. That of tetracontane-12 : 13-dione at 120° involved, during the early stages, the formation of a hydroperoxide (indicated by chemical analyses for active oxygen and by the infrared band at 2·9 μ) which reached its maximum concentration after about 2 hours and then diminished. Infrared spectra of successive samples indicated the disappearance of diketone (band at 13·79 μ) and the formation of carboxylic acid (bands at 3·1, 3·78, and 10·72 μ), the final spectrum closely resembling that of lauric acid. The chemical separation of the reaction product (after 9·5 hours' oxidation) gave (from 100 parts by wt. of starting material) dodecanoic acid, 60; undecanal, 5·7; carbon dioxide, 2·5; tetracontane-12 : 13-dione (recovered), 2·5; unidentified neutral oil, 15; and some water. The spectrum of the neutral oil suggests that it contains an enolic β-diketone grouping (bands at 2·91 and 6·1 μ).[12]

The autoxidation of methyl 9 : 10-dioxostearate (which is, accordingly, an intermediate

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[29] Swern, *J. Amer. Chem. Soc.*, 1948, **70**, 1235.

in the autoxidation of methyl oleate and elaidate) again showed the formation of hydroperoxide during the early stages of reaction and the liberation of some carbon dioxide. The final product contained chiefly nonanoic and azelaic acid.

Analogous results have been reported for the monoketones, di*iso*propyl[30] and di-*n*-propyl ketone.[31] The former gave, in the course of autoxidation, some di*iso*propyl ketone hydroperoxide, butyric acid, acetone, and water. The position of chain scission (between CO and CH_2) is also indicated by other experiments.[32] It is thought therefore that the diketone reacts *via* the hydroperoxide, *e.g.*, as follows:

$$\begin{gathered} CH_3{\cdot}[CH_2]_{10}{\cdot}CO{\cdot}CO{\cdot}CH(O{\cdot}OH){\cdot}[CH_2]_9{\cdot}CH_3 \\ \downarrow \\ CH_3{\cdot}[CH_2]_{10}{\cdot}CO_2H + CO_2 + OHC{\cdot}[CH_2]_9{\cdot}CH_3 \end{gathered}$$

Water may be produced by decomposition of the hydroperoxide to an enolisable triketone.

This tentative scheme would explain the presence of all identified products and could be extended to other diketones.

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[30] Sharp, Patton, and Whitcomb, *J. Amer. Chem. Soc.*, 1951, **73**, 5600.
[31] Sharp, Whitcomb, Patton, and Moorhead, *ibid.*, 1952, **74**, 1802.
[32] Jenkins, *ibid.*, 1935, **57**, 2733; Fuson and Jackson, *ibid.*, 1950, **72**, 1637.