Direct Remote Oxidation of Acyclic Acetates, Macrocyclic Acetates, and Macrolides

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The direct oxidation of acyclic acetates, macrocyclic acetates, and macrolides to mixtures of isomeric monoketo derivatives occurs with varying degrees of regiospecificity.

As part of our general studies on the *direct* remote oxidation of natural product systems [1] we have completed a comparative study of the remote oxidation of

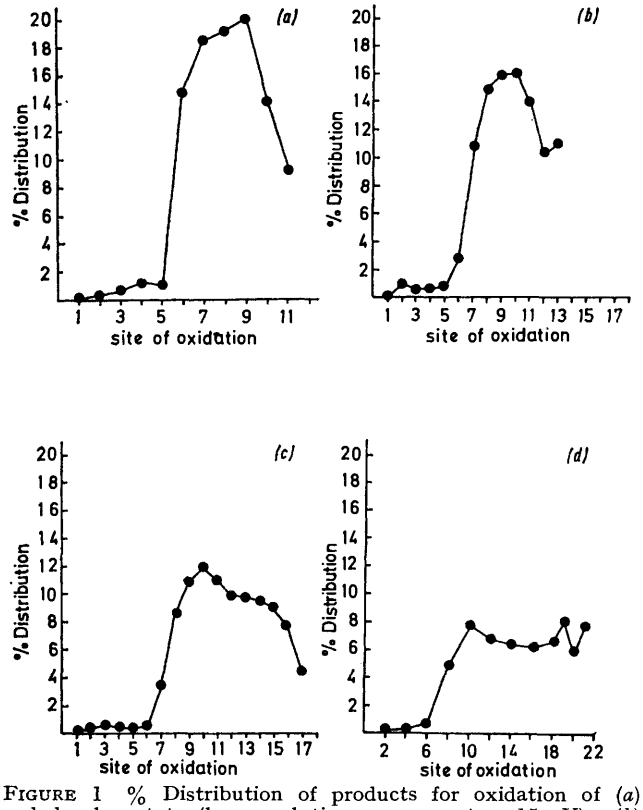


FIGURE 1 % Distribution of products for oxidation of (*a*) dodecyl acetate (low resolution mass spectra, 15 eV); (*b*) tetradecyl acetate (15 eV); (*c*) octadecyl acetate (15 eV; probe temperature, 70°); (*d*) docosyl acetate (15 eV; 150°)

various acyclic and macrocyclic compounds and an outline of our results is provided below.

(a) *Acyclic Acetates* (*Scheme* 1, *Figure* 1).—Our initial investigations [2] in this area involved treatment of pure octadecyl acetate (1; $n = 16$) in acetic acid–acetic anhydride with chromium trioxide–acetic anhydride at room temperature for 48 h. This provided a mixture of monoketoacetates (2; $x + y = 15$) which were separated from starting material and other unidentified products by column chromatography. The yield of product based on consumed starting material was *ca.* 30% and the relative proportions of isomeric monoketoacetates (2; $x + y = 15$) was deduced from the mass spectrum of the ethylene acetals (3; $x + y = 15$) of the corresponding ketoalcohols.† Our results, summarised in Figure 1, clearly demonstrate that octadecyl acetate (1; $n = 16$) can be *directly* oxidised to a mixture of monocarbonyl derivatives and that the process is partially regiospecific. Similar results (Figure 1) were obtained when dodecyl acetate (1; $n = 10$), tetradecyl

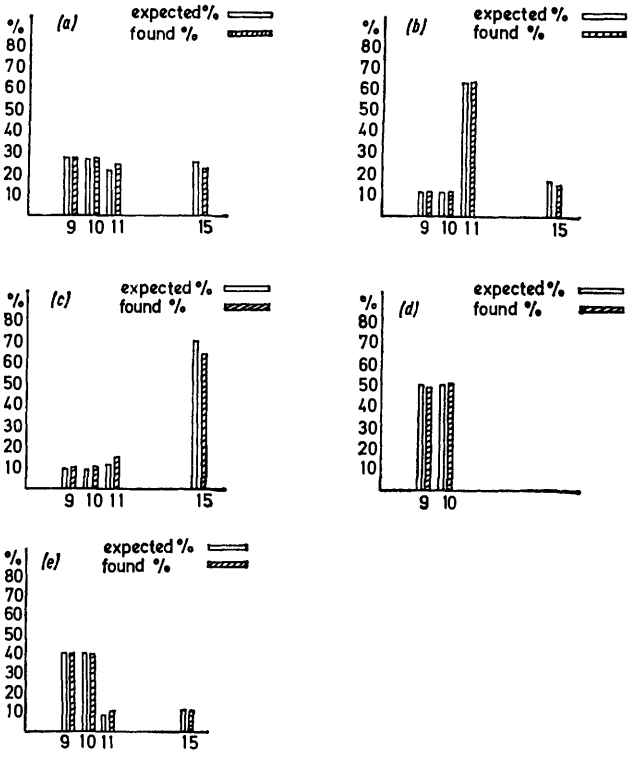
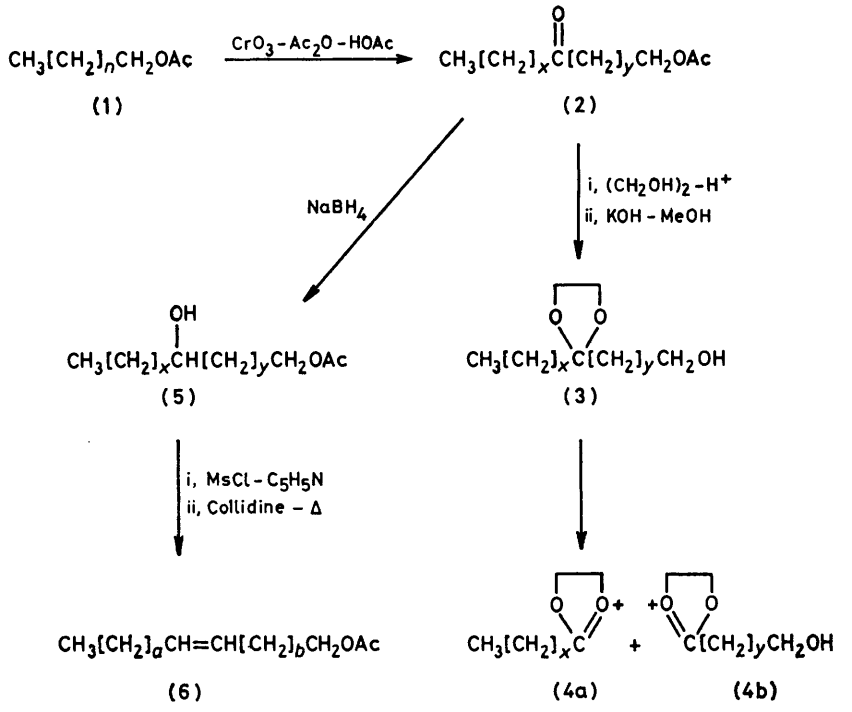


FIGURE 2 Test of reliability of analytical method using mixtures of ethylene acetate from 9-, 10-, 11-, and 15-octadecan-1-ol (low resolution mass spectra, 15 eV; probe temperature, 70°); (*a*) % 9- : 10- : 11- : 15- = 26.4 : 26.4 : 21.7 : 25.4; (*b*) % 9- : 10- : 11- : 15- = 10.3 : 10.3 : 63.0 : 16.4; (*c*) % 9- : 10- : 11- : 15- = 8.9 : 8.9 : 11.0 : 71.2; (*d*) % 9- : 10- = 50 : 50; (*e*) % 9- : 10- : 11- : 15- = 40.5 : 40.5 : 8.3 : 10.8

acetate (1; $n = 12$), and docosyl acetate (1; $n = 20$) were subjected to the same oxidising conditions.‡ As shown in Figure 1, remote oxidation of the acyclic acetates does not occur to any significant extent at positions

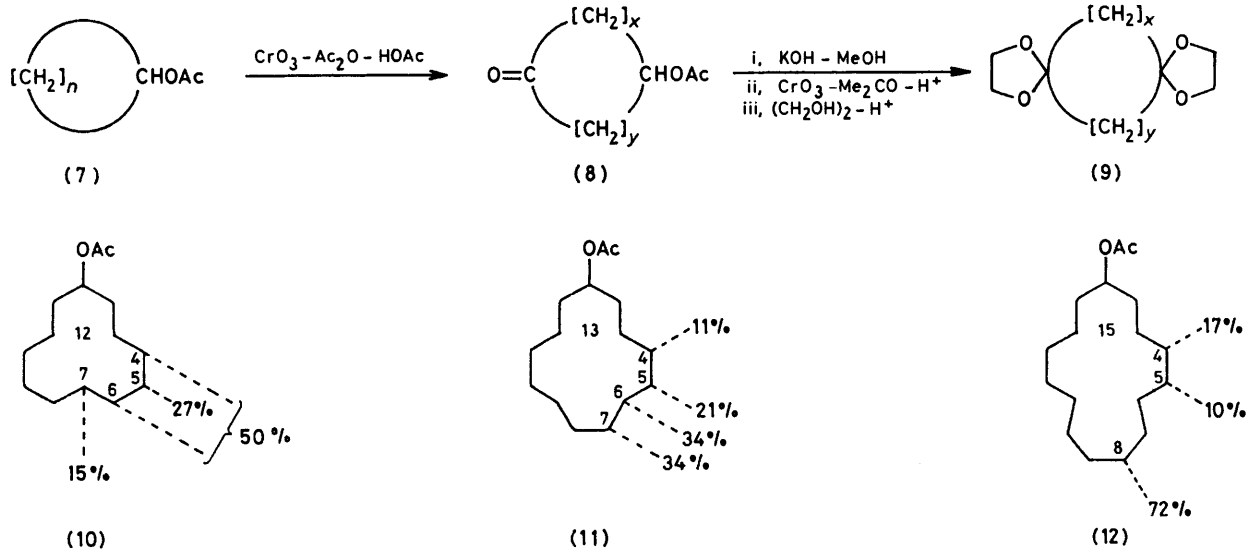
† This analytical method was previously described by Breslow.[3a] The relative amount of each positional isomer was calculated by dividing the sum of the peak heights due to fragments (4a and b) by the sum of the peak heights due to acetal fragments derived from all isomers (*ca.* 90% of total ion current). The reliability of this analytical technique [4] was established by using known mixtures of ethylene acetals derived from synthetic 9-, 10-, 11-, and 15-oxo-octadecan-1-ol (*cf.* Figure 2).

‡ The direct conversion of acyclic acetates to mixtures of monoketoacetates provides a convenient means of preparing mixtures of isomeric alkenyl acetates [*cf.* (6)] for potential use as insect pheromones.[5] This aspect of our remote oxidation studies will be described later.



SCHEME 1

C(2)—C(6) and one reasonable explanation for this effect [6] is that these positions are shielded from reaction by the conformation of the acyclic acetate or a complex formed between the acyclic acetate and oxidising agent.[7] similar transformations can be accomplished in the laboratory with similar efficiency and regiospecificity.† Thus treatment of cyclopentadecyl acetate (7; $n = 14$) in acetic acid–acetic anhydride with chromium trioxide

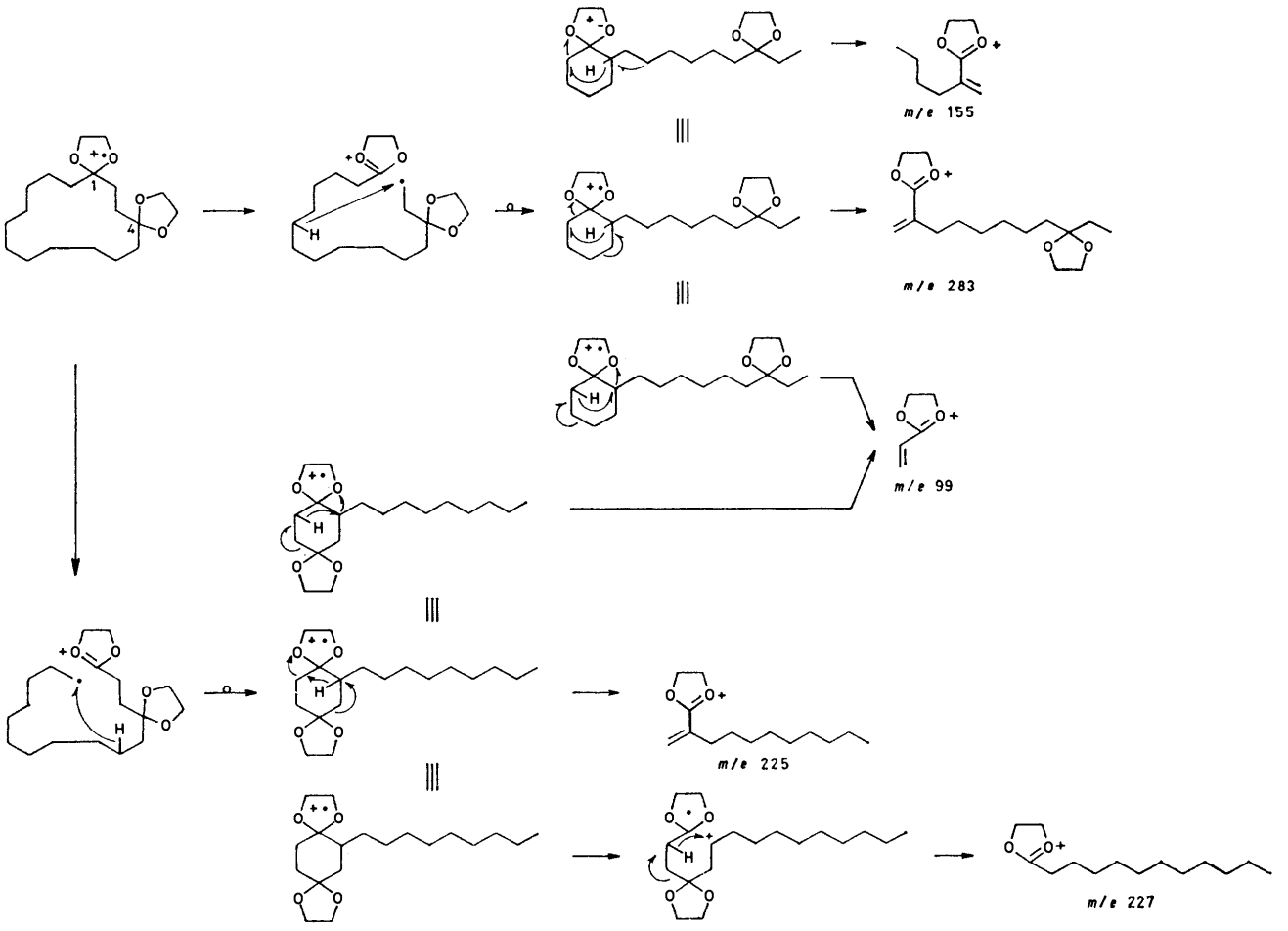


SCHEME 2

(b) *Macrocyclic Acetates* (*Scheme* 2).—Fonken and his associates [8] have shown that cyclododecanol, cyclotridecanol, and cyclotetradecanol are oxidised at C(7), C(6), and, to a much lesser extent, C(5) by *Sporotrichum sulfurescens*. The suggestion was made that all these oxidative transformations could be explained by invoking the intermediacy of an appropriate enzyme–substrate complex. The results outlined below indicate that in acetic anhydride at room temperature for five days provided a mixture of three ketoacetates (8; $x + y = 13$) in 39% yield based on recovered starting material. Hydrolysis and oxidation of the derived ketols gave a

† *Note added in proof.* It has been elegantly demonstrated that remote oxidation of cyclodecyl acetate can be accomplished with greater regiospecificity by the dry ozonation technique (A. L. J. Beckwith and T. Duong, *J.C.S. Chem. Comm.*, 1978, 413).

mixture of diones which were separated by g.l.c. and subsequently converted to the corresponding diacetals (9; $x + y = 13$). Examination of the fragmentation patterns [9] in the mass spectra (15 and 70 eV) of each diacetal led to their identification as the 1,4- 1,5-, and 1,8-isomers (*cf.* Schemes 3—5). The low resolution spectrum of the ' 1,5-diacetal ' was not unique however, since a similar fragmentation pattern could be expected from the 1,7-diacetal (*cf.* Scheme 6). In the latter case, however, the *m/e* 185 peak is probably attributable to a fragment having molecular formula $C_{11}H_{21}O_2$ while in the 1,5-diacetal it would be due to a $C_9H_{13}O_4$ unit. (Scheme 4). Subsequent examination of the high-resolution mass spectrum clearly established that the *m/e* 185 peak was due to the latter fragment. The g.l.c. characteristics of the original ketoacetate mixture indicated that the ratio of 4-, 5-, and 8-oxocyclopentadecyl acetates was 1 : 2 : 7 and therefore the remote oxidation process had occurred with a reasonable degree of regiospecificity. When cyclotridecyl and cyclododecyl acetates were used as substrates similar but less regiospecific oxidative transformations occurred and the ketoacetates were obtained in *ca.* 40% yield. In the case of cyclotridecyl acetate the derived mixture of isomeric diketones could not be completely separated by g.l.c. into its individual components. Instead two fractions were obtained and the mass spectra (15 eV) of the derived diacetals * indicated that one fraction (*ca.* 32%) was a 1 : 2 mixture of 1,4- and 1,5-cyclotridecadione while the other fraction was a 1 : 1 mixture of the 1,6- and 1,7-isomers [*cf.* (11), Scheme 2]. In a similar fashion the diketone mixture derived from remote oxidation of cyclododecyl acetate was separated into three fractions which were identified from the mass spectra of the corresponding diacetals * as cyclododeca-1,5-dione, a mixture of the 1,4- and 1,6-isomers, and cyclodeca-1,7-dione [relative yield; *cf.* (10), Scheme 2].



SCHEME 3

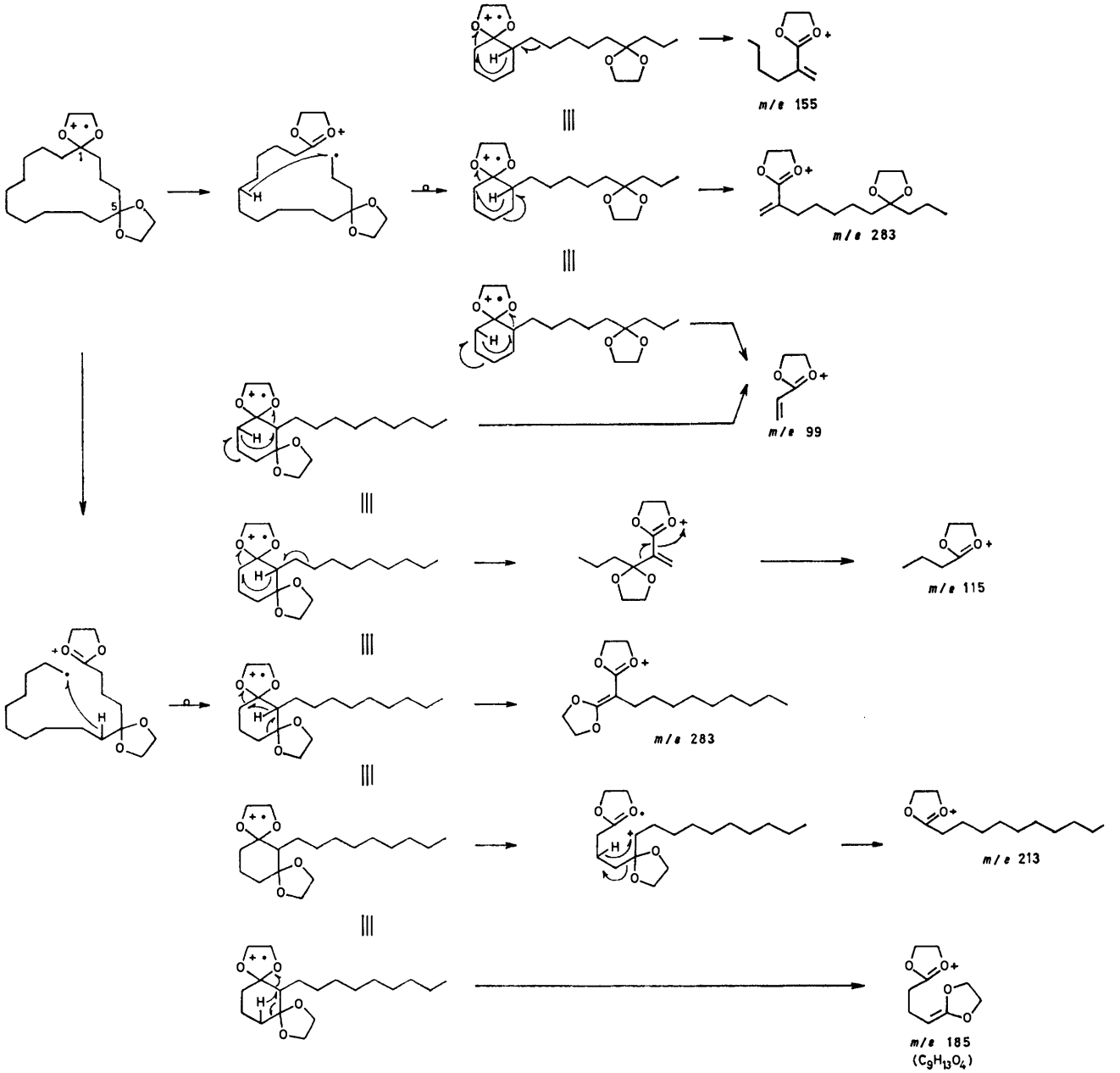
(c) *Macrocyclic Lactones* (*Macrolides*) (*Scheme* 7, *Figure* 3).—Our investigations [10] in this area have been concerned with *direct* remote oxidation of dodecanolide (13; $n = 11$), pentadecanolide (13; $n = 14$), and hexadecanolide (13; $n = 15$).† Treatment of these com-

* Fragmentation mechanisms consistent with the mass spectra of the diacetals derived from cyclododecyl and cyclotridecyl acetate can easily be devised.[9] For the sake of brevity these have not been included in the discussion.

† The common macrolide antibiotics [11] may be regarded as functional derivatives of tridecanolide (14-membered ring) and pentadecanolide. Methymycin is the only well known member of the group based on the undecanolide framework.

pounds with chromium trioxide–acetic anhydride–acetic acid at room temperature for five days provided a mixture of monoketolactones (14; $x + y = 10$, 13, or 14)* which were separated from starting material by column chromatography. The yield of product based on recovered starting material was 33—40% and the relative amount of isomeric monoketolactones was deduced from the mass spectra of the derived hydroxy-acetals (16; $x + y = 10$, 13, or 14) (*cf.* Scheme 7). The results, displayed graphically in Figure 3, clearly indicate that direct remote oxidation of the macrocyclic lactones (13; $n = 11$, 14, and 15) occurs with a reasonably high degree of regiospecificity.

A proper explanation for the results described above is not yet available. It seems reasonable to suggest, however, that complex formation between the oxidising agent (chromyl acetate) and the functional group of the substrate (acyclic or macrocyclic acetate) may be responsible for imposing limitations on the number of possible reaction sites.[3b,6,7]



SCHEME 4

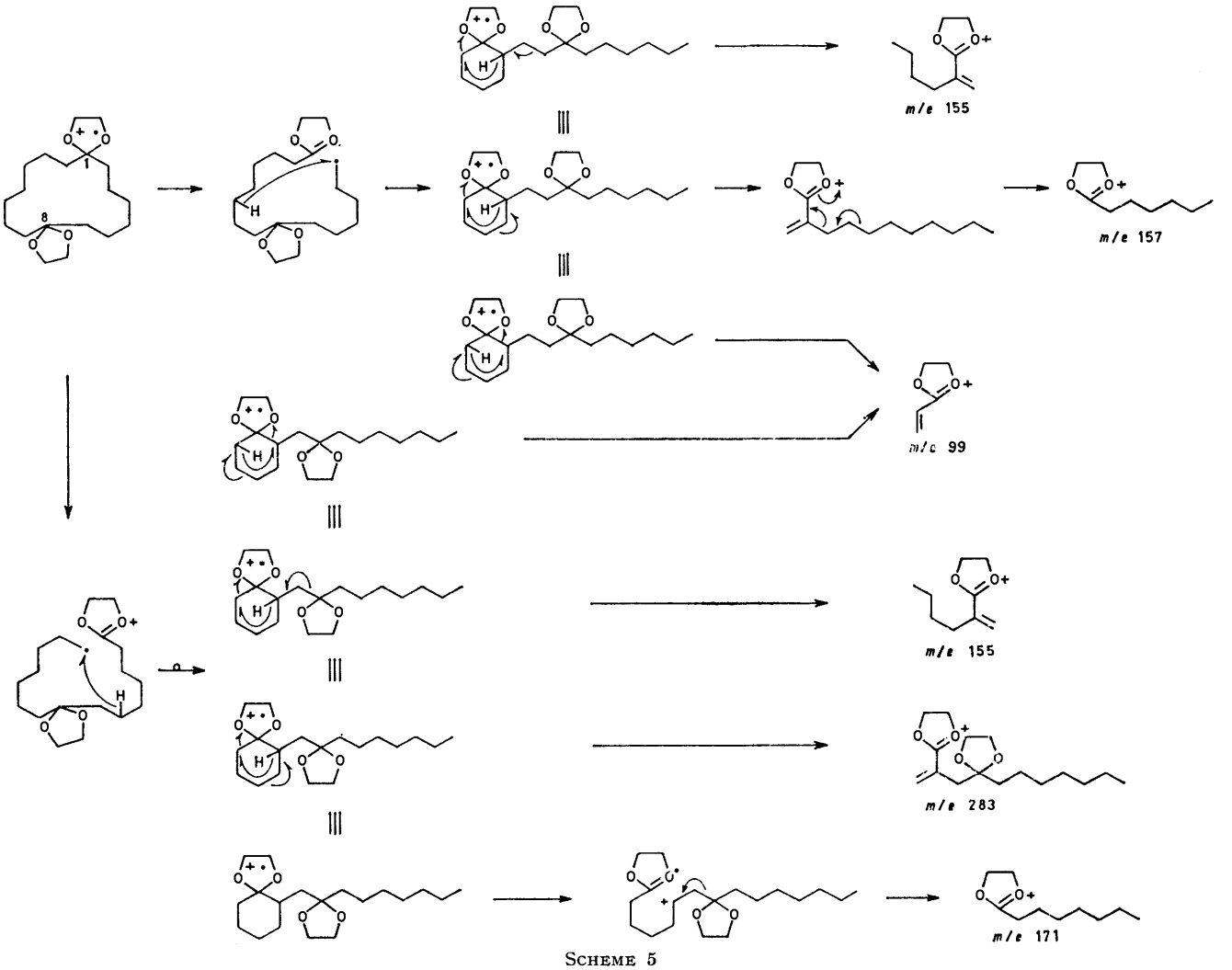
* Reduction and dehydration of the monoketohexadecanolides (14; $x + y = 14$) provided a mixture of ambrettolide (18; $a = 5$, $b = 8$) [12] and its positional isomers. This mixture will be evaluated for insect pheromone activity.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus. G.l.c. was carried out on Varian Aerograph 90-P, Perkin-

Elmer 900, and Hewlett–Packard 5830A instruments. Routine i.r. spectra were recorded on Perkin-Elmer Infracord 137 and 710A spectrophotometers. 60 MHz N.m.r. spectra were recorded on a Varian A-60 or T-60 instrument and 100 MHz spectra on a Varian HA-100 or XL-100 instrument (tetramethysilane as internal reference). Mass spectra were recorded on A.E.I. MS902 and Atlas CH-4 spectrometers. Microanalysis were performed by Mr. P. Borda.

Oxidation of Octadecyl Acetate (1; $n = 16$).—Chromium trioxide (7 g) in acetic anhydride (14 ml) was added dropwise to a cold mixture of octadecyl acetate (1; $n = 16$) (5 g, 0.016 mol) in glacial acetic acid (20 ml) and acetic anhydride (9 ml) over 1.5 h. After stirring at room temperature for five days, water was cautiously added to the mixture. Excess of acetic anhydride was removed under reduced pressure and the resulting green solution was shaken with enough ether until an organic layer was present. The whole mixture was then filtered through a thin layer of Celite and extracted with ether (5×). The combined extracts were washed successively with 2N-sodium hydroxide (2×), saturated sodium hydrogencarbonate solution (4×), and water (2×). After drying ($MgSO_4$), removal of solvent provided a yellow solid (3.2 g) which was shown by g.l.c. (3% SE30) to consist of octadecyl acetate (28%), a mixture of keto-octadecyl acetates (59%) (unresolved on g.l.c.), and a mixture of polyketo-octadecyl acetates (13%). Careful column chromatography of the mixture over Woelm silica gel grade III gave, by elution with light petroleum–ether (98 : 2), a mixture of keto-octadecyl acetates (2; $x + y = 15$) (1.33 g, 31% based on consumed starting material), $\nu_{max.}$ (CCl_4) 1 737, 1 715, and 1 232 cm^{-1}; τ(CCl_4; 60 MHz) 6.00 (2 H, t, CH_2OAc), 7.70 (4 H, t, CH_2COCH_2), 8.02 (3 H, s, O_2CCH_3), 8.70br (26 H, s, 13 CH_2), and 9.10 (3 H, t, $CH_3[CH_2]_n$); *m/e* 326 (M^+) (Found: C, 73.65; H, 11.55. Calc. for $C_{20}H_{38}O_3$: C, 73.55; H, 11.75%).



SCHEME 5

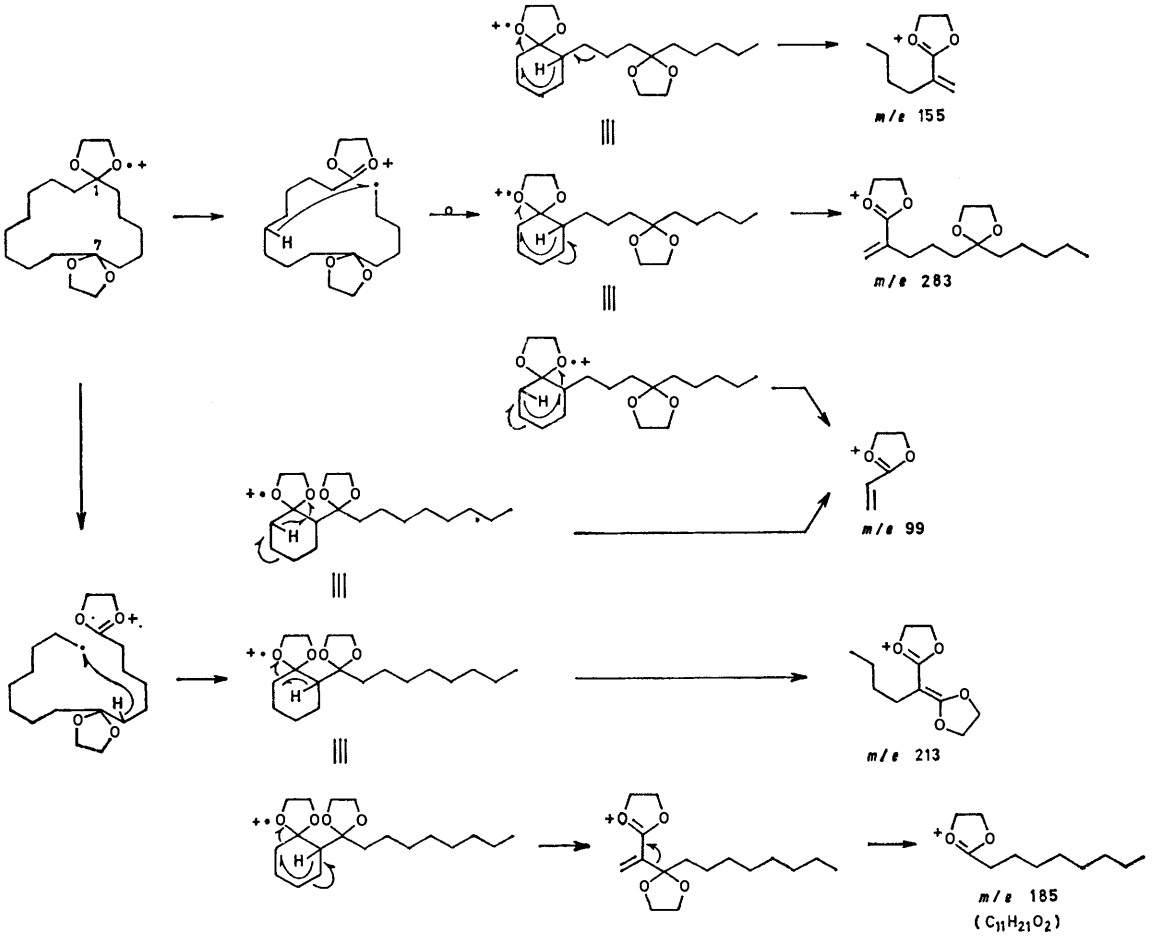
Ethylene Acetals of Keto-octadecyl Acetates.—Ethyl orthoformate (0.8 ml), ethylene glycol (0.2 ml), and toluene-*p*-sulphonic acid (19 mg) were added to a mixture of keto-octadecyl acetates (400 mg). After 6 h at 90 °C, the solution was heated at 150 °C for 2 h to remove excess of ethyl orthoformate. After cooling, saturated sodium hydrogencarbonate solution was added and the solution extracted with ether (3×). The combined extracts were washed with saturated sodium chloride solution and worked up in the usual way to provide a yellow oil (378 mg) which was shown by g.l.c. (3% SE30) to consist of a small amount of

keto-octadecyl acetates and a mixture of keto-octadecyl acetate ethylene acetals. Column chromatography (Woelm silica gel, grade III) gave, by elution with light petroleum–ether, a mixture of keto-octadecyl acetate ethylene acetals (300 mg), $\nu_{max.}$ (CCl_4) 1 748, 1 232, and 1 070 cm^{-1}; τ(CCl_4; 60 MHz) 6.04 (2 H, t, CH_2OAc), 6.20 (4 H, s, OCH_2CH_2O), 8.06 (3 H, s, $OCOCH_3$), 8.72br (30 H, s, 15 CH_2), and 9.13 (t, 3 H, $CH_3[CH_2]_n$).

Keto-octadecanol Ethylene Acetals (3; $x + y = 15$).— Sodium hydroxide (30 mg), methanol (5 ml), and keto-octadecyl acetate acetals (126 mg) were heated at 100 °C for 5 h. Methanol was then removed by distillation and the residue diluted with water and extracted with ether (4×). The combined extracts were washed with saturated sodium chloride solution (3×), water (2×), and dried ($MgSO_4$). Removal of solvent provided (3; $x + y = 15$) as a pale yellow oil (118 mg), $\nu_{max.}$ (CCl_4) 3 400 and 1 070 cm^{-1}; τ(CCl_4; 60 MHz) 6.20 (4 H, s, OCH_2CH_2O), 6.50 (2 H, t, CH_2OH), 8.72br (30 H, s, 15 CH_2), and 9.10 (3 H, t, $CH_3[CH_2]_n$) (Found: C, 72.6; H, 12.1. Calc. for $C_{20}H_{40}O_3$: C, 73.1; H, 12.25%).

Oxidation of Dodecyl, Tetradecyl, and Docosyl Acetates.— The oxidation of dodecyl, tetradecyl, and docosyl acetate was carried out as described for octadecyl acetate. Satisfactory analytical and spectroscopic data were obtained for the oxidation products and the ethylene acetal derivatives of the derived ketols.

Oxidation of Cyclopentadecyl Acetate (7; $n = 14$).— Chromium trioxide (7 g) in acetic acid (14 ml) was added dropwise to a cold mixture of cyclopentadecyl acetate (5 g, 0.019 mol) in glacial acetic acid (20 ml) and acetic anhydride (9 ml). The mixture was stirred at room temperature for five days. Water (200 ml) was then added and the excess of acetic anhydride was removed. The mixture was extracted with ether (6×). The combined extracts were washed successively with saturated sodium hydrogencarbonate solution (4×) and water (2×) and dried ($MgSO_4$). Removal of solvent provided a yellow oil (3.2 g)



SCHEME 6

which was shown by g.l.c. (3% SE30) to consist of cyclopentadecyl acetate (35%), a mixture of ketocyclopentadecyl acetates (54.5%) (unresolved on g.l.c.), and a mixture of polyketocyclopentadecyl acetates (10.5%). Column chromatography of the mixture over Woelm silica gel (grade III) gave, by elution with light petroleum–ether, a mixture of ketocyclopentadecyl acetates (9; $x + y = 13$) (1.73 g, 39.2% based on consumed starting material), $\nu_{max.}$ (CCl_4) 1 745, 1 720, and 1 245 cm^{-1}; τ(CCl_4; 100 MHz) 5.27 (1 H, m, $CHOAc$), 7.66 (4 H, mixed t, CH_2COCH_2), 8.06, 8.08 (3 H, s, $OCOCH_3$), 8.42, and 8.70br (22 H, s, 11 CH_2) (Found: C, 72.6; H, 10.65. Calc. for $C_{17}H_{30}O_3$: C, 72.3; H, 10.7%).

Hydroxycyclopentadecanones.—A mixture of acetoxycyclopentadecanones (690 mg) and potassium hydroxide (246 mg) in methanol (20 ml) was refluxed overnight.

After removal of solvent the residue was diluted with water and extracted with ether (4×). Work-up in the usual way provided a mixture of isomeric hydroxycyclopentadecanones as a yellow solid (559 mg), $\nu_{max.}$ (CCl_4) 3 600 and 1 725 cm^{-1}; τ(CCl_4; 100 MHz; D_2O added) 6.44 (1 H, m, C*H*OH), 7.65 (4 H, mixed t, CH_2COCH_2), 8.39, and 8.70br (22 H, s, 11 CH_2).

Cyclopentadecane-1,x-diones.—Jones reagent (CrO_3–H_2SO_4–H_2O) (3 ml) was added dropwise to a solution of hydroxycyclopentadecanones (300 mg) in acetone (5 ml) until oxidation was complete. The mixture was diluted with water (25 ml), extracted with ether (3×), and the combined ether extracts washed with saturated sodium hydrogencarbonate (2×) and water (2×) and dried ($MgSO_4$). Removal of solvent provided a pale yellow solid (254 mg) which was shown by g.l.c. (20% DEGS, 10% FFAP, 5% OV210) to consist of cyclopentadecane-1,4-dione (10%), cyclopentadecane-1,5-dione (18%), and cyclopentadecane-1,8-dione (72%). Preparative g.l.c. of the mixture (20% DEGS column at 200 °C) gave the pure diones as white solids, $\nu_{max.}$ (CCl_4) 1 720 cm^{-1}; τ(CCl_4; 100 MHz) 7.69 (8 H m, $[CH_2COCH_2]_2$), 8.41 (8 H, m, $[CH_2CH_2COCH_2CH_2]_2$), and 8.77br (10 H, s, 5 CH_2); *m/e* 238 (M^+).

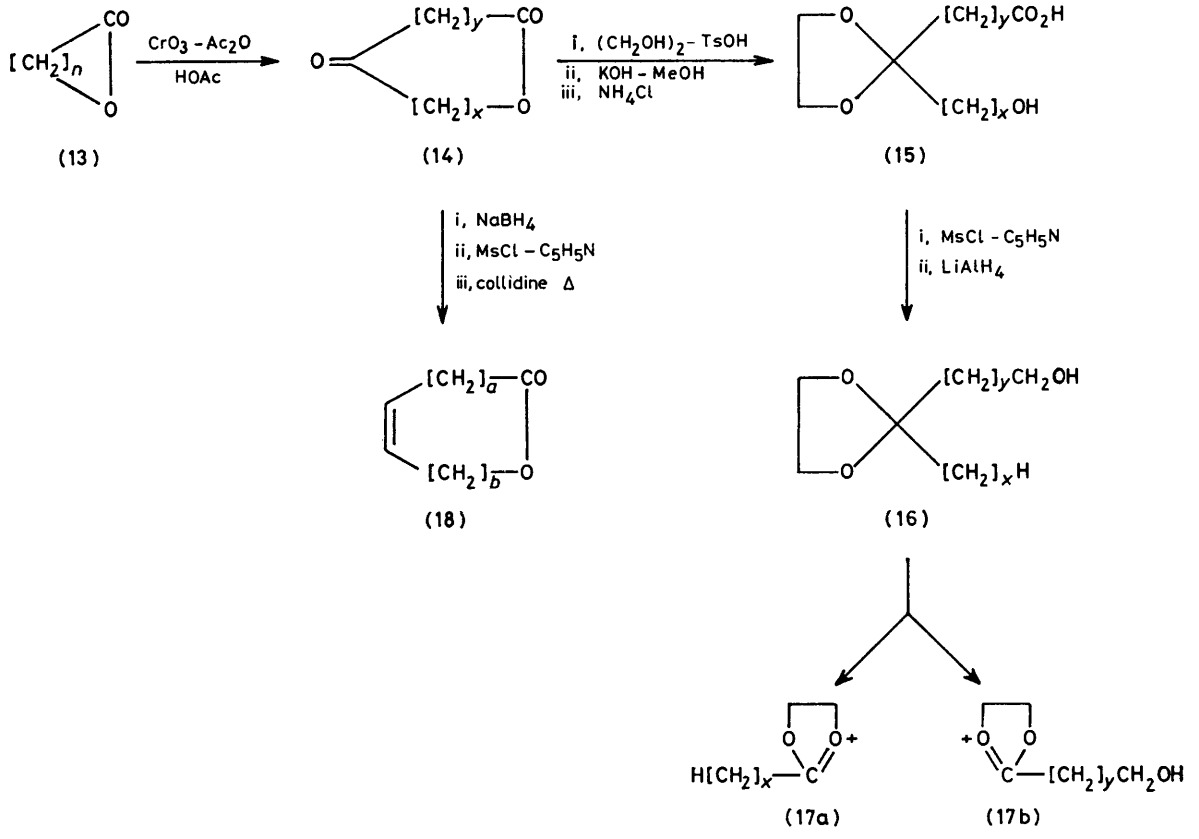
Bisethylene Acetal of Cyclopentadecane-1,4-dione (9; *x* = 2, *y* = 11.—A mixture of cyclopentadecane-1,4-dione (19 mg), dry ethylene glycol (0.1 ml), and toluene-*p*-sulphonic acid monohydrate (5 mg) in dry benzene (20 ml) was refluxed for 10 days using a Dean–Stark water separator. The resulted mixture was washed with saturated sodium hydrogencarbonate solution (2×) and water (1×) and dried ($MgSO_4$). Removal of solvent provided a white solid (26 mg) which was chromatographed on Woelm silica gel (grade III). Elution with 5% ether–light petroleum provided pure *bisethylene acetal* of *cyclopentadecane-1,4-dione* (17.6 mg), $\nu_{max.}$ (CCl_4) 1 080 and 1 100 cm^{-1}; τ(CCl_4; 60 MHz) 6.23 (8 H, s, $[OCH_2CH_2O]_2$), 8.47 (8 H, s, 4 CH_2), and 8.63br (18 H, s, 9 CH_2); *m/e* 326 (M^+) (Found: C, 69.5; H, 10.75. $C_{19}H_{34}O_4$ requires C, 69.9; H, 10.5%).

Bisethylene Acetal of Cyclopentadecane-1,5-dione (9; *x* = 3, *y* = 10).—Cyclopentadecane-1,5-dione was converted to the diacetal as described for cyclopentadecane-1,4-dione, $\nu_{max.}$ (CCl_4) 1 080 and 1 100 cm^{-1}; τ(CCl_4; 60 MHz) 6.20 (8 H, s, $[OCH_2CH_2O]_2$) and 8.63br (26 H, s, 13 CH_2); *m/e* 326 (M^+).

Bisethylene Acetal of Cyclopentadecane-1,8-dione (9; *x* = 6, *y* = 7).—Cyclopentadecane-1,8-dione was converted to the diacetal as described for cyclopentadecane-1,8-dione, $\nu_{max.}$ (CCl_4) 1 090 cm^{-1}; τ(CCl_4; 60 MHz) 6.23 (8 H, s, $[CH_2CH_2O]_2$), and 8.60br (26 H, s, 13 CH_2); *m/e* 326 (M^+) (Found: C, 69.75; H, 10.2. $C_{19}H_{34}O_4$ requires C, 69.9; H, 10.5%).

Oxidation of Cyclotridecyl and Cyclododecyl Acetate.—The procedure used for the oxidation of cyclotridecyl and cyclododecyl acetate was identical to that described for cyclopentadecyl acetate. Satisfactory analytical and spectroscopic data were obtained for the oxidation products and the bisethylene acetals of the corresponding diketones.

Oxidation of 16-*Hexadecanolide* (13; n = 15).—Chromium trioxide (7.6 g) in acetic anhydride (16 ml) was added dropwise to a cold mixture of 16-hexadecanolide (5.8 g, 0.023 mol) in glacial acetic acid (20 ml) and acetic anhydride (9 ml). The mixture was stirred at 0—5 °C for 3 h and



SCHEME 7

then at room temperature for five days. Water (200 ml) was added and excess of acetic anhydride was removed. The mixture was extracted with ether (6×) and the combined extracts washed successively with saturated sodium hydrogencarbonate solution (4×) and water (2×) and dried ($MgSO_4$). Removal of solvent provided a yellow oil (3.6 g) which was shown by g.l.c. (3% SE30) to consist of 16-hexadecanolide (34%), a mixture of *x*-oxo-16-hexadecanolides (62%) (unresolved on g.l.c.) and a mixture of polyoxo-16-hexadecanolides (4%). Column chromatography of the mixture over Woelm silica gel (grade III) gave, by elution with light petroleum (b.p. 30—60 °C)–ether, a mixture of *x*-oxo-16-hexadecanolides (14; $x + y = 14$) (1.72 g, 33% based on consumed starting material),

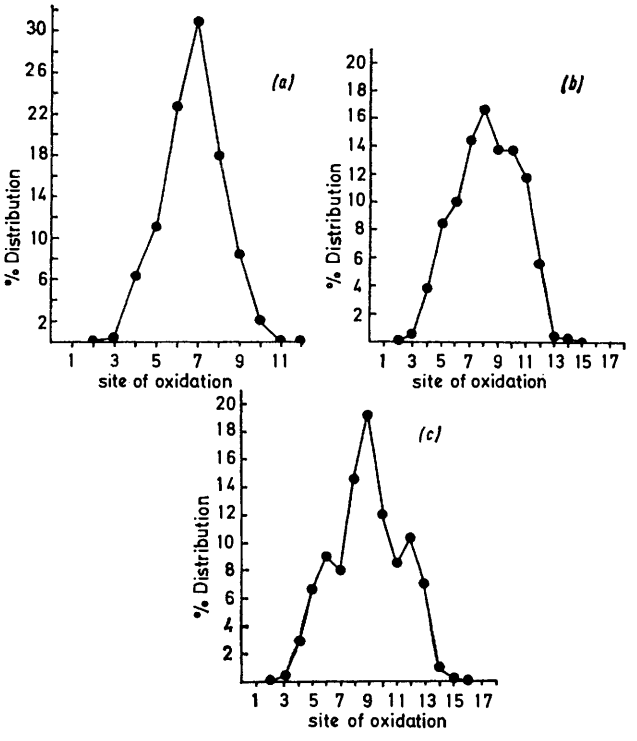


FIGURE 3 % Distribution of products for oxidation (low-resolution mass spectra, 15 eV; probe temperature, 70°) of: (*a*) dodecanolide; (*b*) pentadecanolide; (*c*) hexadecanolide

$\nu_{max.}$ (CCl_4) 1 738, 1 720, 1 250, and 1 175 cm^{-1}; τ(CCl_4; 100 MHz) 5.97 (2 H, t, $COOCH_2$), 7.72 (6 H, mixed t, CH_2COCH_2, CH_2COO), 8.42, 8.70br (20 H, s, 10 CH_2) (Found: C, 71.45; H, 10.25. Calc. for $C_{16}H_{28}O_3$: C, 71.6; H, 10.5%).

Acetals of x-*oxo*-16-*hexadecanolides*.—A mixture of *x*-oxo-16-hexadecanolides (361 mg), ethylene glycol (0.4 ml), and toluene-*p*-sulphonic acid monohydrate (15 mg) in benzene (30 ml) was refluxed for four days and water was removed by a Dean–Stark water separator. The resulting mixture was cooled and washed with saturated sodium hydrogencarbonate solution (2×) and water (1×) and dried ($MgSO_4$). Removal of solvent provided a yellow oil (371 mg) which was chromatographed on alumina (grade IV); pentane eluted the pure acetals of *x*-oxo-16-hexadecanolides (275 mg), $\nu_{max.}$ (CCl_4) 1 738, 1 240, 1 150, and 1 075 cm^{-1}; τ(CCl_4; 60 MHz) 5.97 (2 H, t, $COOCH_2$), 6.23 (4 H, s, OCH_2CH_2O), 7.80 (2 H, t, CH_2COO), 8.40, and 8.67br (24 H, s, 12 CH_2).

Acetals (15; x + y = 14) *of* x-*oxo*-16-*hydroxyhexadecanoic Acids*.—A mixture of *x*-keto-16-hexadecanolide acetals (160 mg) and potassium hydroxide (41 mg) in methanol (4 ml) was refluxed overnight and then acidified to pH 6. The mixture was extracted with ether (5×). The combined ether extracts were washed with water (1×) and dried ($MgSO_4$). Removal of solvent provided acetals (15; $x + y = 14$) as a yellow oil (130 mg), $\nu_{max.}$ (CCl_4) 3 400, 3 000—2 500, 1 715, and 1 075 cm^{-1}; τ(CCl_4; 60 MHz) 3.65, (2 H, s, COOH, OH), 6.07 (4 H, s, OCH_2CH_2O), 6.37 (2 H, t, CH_2OH), 7.65 (2 H, t, CH_2COOH), and 8.57br (24 H, s, 12 CH_2).

Acetals (16; x + y = 14) *of* x-*oxohexadecanols*.—Mesyl chloride (0.05 ml) was added to a solution of the acetals (15; $x + y = 14$) of *x*-oxo-16-hydroxyhexadecanoic acids in dry pyridine (0.21 ml) at 0—5 °C. After stirring at room temperature for 2 h, the solution was diluted with water (5 ml) and extracted with methylene chloride (3×). The combined methylene chloride extracts were washed with saturated ammonium chloride solution and water and dried ($MgSO_4$). Removal of solvent provided a yellow oil (119 mg) which was dissolved in dry tetrahydrofuran (10 ml) and added to a mixture of lithium aluminium hydride (127 mg) in dry ether (25 ml). After stirring and refluxing for 2.5 h, excess of lithium aluminium hydride was destroyed by addition of water. The mixture was then treated with 2N-sodium hydroxide solution and water and filtered. The filtrate was extracted with ether (3×) The combined ether extracts were washed with saturated ammonium chloride solution and water and dried ($MgSO_4$) Removal of solvent provided a yellow-brown oil (72 mg) which, after column chromatography on alumina [grade IV; elution with 10% ether–light petroleum (b.p. 30—60 °C)] gave the acetals (16; $x + y = 14$) as a yellow oil (55 mg), $\nu_{max.}$ (CCl_4) 3 400, 1 075, and 1 050 cm^{-1}; τ(CCl_4; 100 MHz) 6.22 (4 H, s, OCH_2CH_2O), 6.52 (2 H, t, CH_2OH), 8.58, 8.76br (26 H, s, 13 CH_2), and 8.14 (3 H, t, $CH_3[CH_2]_n$).

Oxidation of 15-*Pentadecanolide and* 12-*Dodecanolide*.—The oxidation procedure was identical to that described for 16-hexadecanolide. Satisfactory analytical and spectroscopic data were obtained for the oxidation products and the ethylene acetals of the derived straight-chain ketols.

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