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FATTY ACIDS, PART 5 *: A STUDY OF THE OXYMERCURATION-DEMERCURATION REACTION OF SOME C_{11}-UNSATURATED FATTY ESTERS AND METHYL OCTADEC-*CIS*-10-EN-5-YNOATE

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The methoxymercuration-demercuration reactions of all the methyl *cis*-undecenoates are reported. Oxymercuration reaction of acetylenic esters gives keto- and hydroxy-esters when demercurated with hydrochloric acid and sodium borohydride respectively. Similar reactions are carried out with methyl octadec-*cis*-10-en-5-ynoate, which give the methyl 5(6)-oxooctadec-*cis*-10-enoate and 5(6)-hydroxy-10(11)-methoxyoctadecanoate isomers.

Reduction of the methyl 5(6)-oxooctadec-*cis*-10-enoates with sodium borohydride yields the corresponding methyl hydroxy-esters, which on treatment with mercuric acetate (in methanol) and demercurated with sodium borohydride give methyl 5-hydroxy-10(11)-methoxyoctadecanoates and the 2,6-disubstituted tetrahydropyranyl derivative, methyl 6,10-epoxyoctadecanoate.

I. Introduction

Since the discovery of the oxymercuration of olefins by Hofmann and Sand [1], solvomercuration-demercuration reactions of ethylenic compounds have been intensively studied in recent years [2]. Olah and Clifford [3] have now confirmed the existence of the mercurium ion intermediate by their ^1H and ^{13}C NMR studies of mercurated olefins. However, no similar studies have yet been carried out on the mercurated intermediacy of non-terminal acetylenes, although 1-alkynes are reported to give stable dialkynylmercury compounds on treatment with mercury salts [4]. Application of the oxymercuration-demercuration reaction to long-chain ethylenic fatty acids and alcohols was conducted by Gunstone and Inglis [5], and double bond location in unsaturated fatty acids was determined by similar methods by McQuillin et al. [6]. Though mercuric acetate is widely used in separating saturated and ethylenic fatty acids [7], the possibility of separation of long chain non-terminal acetylenic fatty acids by this technique has not been exploited.

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Oxymercuration-demercuration reactions of acetylenes have received comparatively little attention. Some Russian workers [8] have investigated the addition reaction of various acetylenic compounds, and more recently Hudrlik and Hudrlik [9] have made use of the value of the oxymercuration-demercuration reaction with sodium borohydride in their preparation of enol acetates and enol ethers. Seher [10] reported the results of the mercuration reaction of the octadec-9-ynoic acid and that of a C_{22}-conjugated diacetylenic diester.

This paper reports the methoxymercuration-demercuration reaction of all isomeric methyl *cis*-undecenoates, describes the preparative value of the oxymercuration-demercuration reaction of some C_{11}-acetylenic esters with hydrochloric acid and sodium borohydride, and describes an application of the results to methyl octadec-*cis*-10-en-5-ynoate.

II. Results and discussion

A. *Methoxymercuration-demercuration of all the methyl* cis-*undecenoates [11]*

Table 1 contains a summary of our experiments on the methoxymercuration-demercuration of these isomers of methyl *cis*-undecenoates. The results with Δ2–Δ7*c* esters reconfirm that already reported by Gunstone and Inglis [5]. The Δ2*c* esters give entirely the methyl 3-methoxyundec anoate; Δ3*c* and Δ4*c* esters give predominantly the 4-methoxy and 5-methoxyundecanoate as the ester function exerts an orienting influence on the attacking methoxyl group; while Δ5*c*, Δ6*c* and Δ7*c* esters furnish equal amounts of 5(6)-, 6(7)- and 7(8)-methoxyundecanoate isomers, indicating that the ester and the methyl group at the termini of the chain have no directing influence on the incoming methoxyl group during the mercuration reaction.

Table 1
Methoxymercuration-demercuration of methyl *cis*-undecenoates.

Isomer	Products (%, ECL Silar 10C)	
Δ2*c*	3 OMe (95%, 13.5)	
Δ3*c*	3 OMe (5%, 13.5)	4 OMe (95%, 13.9)
Δ4*c*	4 OMe (26%, 13.9)	5 OMe (74%, 14.3)
Δ5*c*	5 OMe (50%, 14.4)	6 OMe (50%, 14.4)
Δ6*c*	6 OMe (50%, 14.4)	7 OMe (50%, 14.4)
Δ7*c*	7 OMe (50%, 14.5)	8 OMe (50%, 14.5)
Δ8*c*	8 OMe (36%, 14.5)	9 OMe (64%, 14.8)
Δ9*c*	9 OMe (3%, 14.8)	10 OMe (97%, 15.1)
Δ10*e*	10 OMe (100%, 15.1)	

The Δ10*e* ester gives exclusively methyl 10-methoxyundecanoate resulting from Markownikov addition [5]. The inductive effect of the terminal group also influences the addition of the methoxyl group during the methoxymercuration reaction of the Δ8*c* and Δ9*c* esters. With these two alkenoates the methoxy group is attached preferentially to the unsaturated carbon atom nearer to the methyl group. The Δ9*c* esters give 97% of the 10-methoxyundecanoate (3% 9-methoxy), while the Δ8*c* esters furnish 64% of the 9-methoxyundecanoate (36% 8-methoxy).

The NMR and MS results of the products from the methoxymercuration-demercuration reactions of all the methyl *cis*-undecenoates are summarised in tables 2 and 3.

B. Oxymercuration-demercuration reaction of methyl 9- and 10-undecynoates

1. With hydrochloric acid

Treatment of the intermediate mercury compound of the Δ9*a* and Δ10*a* ester with hydrochloric acid does not regenerate the acetylenic ester as in the case of ethylenic esters, but produce instead the corresponding methyl 9(10)- and 10-keto-esters (93 and 97% yield) respectively. Contrary to the Markownikov rule the Δ9*a* esters give methyl 9(10)-oxoundecanoate in approximately 1 : 1 ratio (47% 9-oxo and 53% 10-oxoundecanoate by GLC).

2. With sodium borohydride

Reaction of the intermediate mercury compound of the Δ9*a* and Δ10*a* esters with excess aqueous sodium borohydride solution gives the 9(10)- and 10-hydroxyundecanoate (96 and 58% yield) respectively. It is noteworthy to point out again that the Δ9*a* esters give an approximately 1 : 1 proportion of the 9- and 10-hydroxyundecanoate (from MS analysis by comparison of peak intensities of the major fragments) suggesting that the inductive effect of the terminal methyl group has no significant orienting influence on the attacking group. Oxidation of the 9(10)-hydroxyundecanoate provides 9(10)-oxoundecanoate, which can be readily separated on GLC (46% 9-oxo and 54% 10-oxoundecanoate) reconfirming the preceeding observation.

However, when duplicate oxymercuration-demercuration reaction products of the same alkynoates are immediately extracted after the addition of sodium borohydride, the Δ9*a* and Δ10*a* esters give methyl oxoundecanoate (50% and 30% yield respectively by GLC), indicating the presence of the keto-ester intermediate after initial demercuration with sodium borohydride prior to further reduction to the hydroxyundecanoates in excess borohydride.

In summing up: ethylenic esters are regenerated from their oxymercurated intermediates by hydrochloric acid, while mercurated acetylenic esters give oxo-derivatives. When sodium borohydride is used as the demercurating agent, methoxyl groups are added on to the double bond of ethylenic esters, while hydroxy esters are obtained from acetylenic esters.

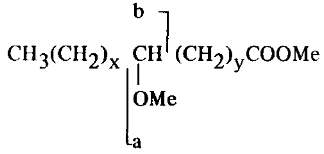
Table 2
NMR (chemical shift τ) of products from methoxymercuration-demercuration of all methyl *cis*-undecenoates.

Substrate	Products	Chemical shift (τ)				
		$C\underline{H}_3-$	$-(C\underline{H}_2)_n-$	$-C\underline{H}_2COOMe$	$C\underline{H}_3OC\underline{H}<$	$-COOC\underline{H}_3$
Δ2*c*	3 OMe	9.12 (~3H)	8.72 (~14H)	7.49 (2H)	6.60 (~3H) 6.68 (~1H)	6.32 (3H)
Δ3*c*	3(4) OMe	9.11	8.69	7.60	6.60 (~3H) 6.70 (~1H)	6.33
Δ4*c*	4(5) OMe	9.11	8.69	7.65	6.69 (4H)	6.36
Δ5*c*	5(6) OMe	9.10	8.75	7.58	6.69	6.32
Δ6*c*	6(7) OMe	9.10	8.61	7.68	6.69	6.35
Δ7*c*	7(8) OMe	9.09	8.72	7.67	6.68	6.30
Δ8*c*	8(9) OMe	9.08 (~3H) 8.95 (~3H)	8.62	7.69	6.69	6.33
Δ9*c*	9(10) OMe	8.90	8.70	7.70	6.70	6.34
Δ10*e*	10 OMe	8.90	8.70	7.70	6.70	6.35

Table 3

Mass spectra (70 eV) of methoxymercuration-demercuration products of all the methyl *cis*-undecenoates. Values quoted are *m/e* of the major fra fragments and intensity relative to the base peak = 100.

methyl methoxyundecanoate:

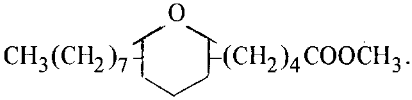


$CH_3(CH_2)_x\underset{\underset{a}{|}}{\overset{b}{\overset{|}{CH}}}(OMe)(CH_2)_yCOOMe$

Substrate	Product		M−31	a	a−32	b	other
Δ2*c*	3 OMe	(x = 7, y = 1)	199 (2)	117 (100)	85 (24)	157 (54)	75 (100)
Δ3*c*	3 OMe		199 (1)	117 (0.8)	85 (11)	157 (2)	71 (100)
	4 OMe	(x = 6, y = 2)		131 (66)	99 (20)	143 (9)	
Δ4*c*	4 OMe		199 (1)	131 (24)	99 (7)	143 (5)	71 (100)
	5 OMe	(x = 5, y = 3)		145 (44)	113 (33)	129 (22)	
Δ5*c*	5 OMe		199 (4)	145 (61)	113 (36)	129 (36)	71 (100)
	6 OMe	(x = 4, y = 4)		159 (43)	127 (68)	115 (46)	
Δ6*c*	6 OMe		199 (5)	159 (47)	127 (66)	115 (80)	
	7 OMe	(x = 3, y = 5)		173 (23)	141 (32)	101 (100)	
Δ7*c*	7 OMe		199 (2)	173 (25)	141 (20)	101 (63)	81 (100)
	8 OMe	(x = 2, y = 6)		187 (15)	155 (11)	87 (55)	
Δ8*c*	8 OMe		199 (4)	187 (23)	155 (3)	87 (65)	
	9 OMe	(x = 1, y = 7)		201 (25)	169 (7)	73 (100)	
Δ9*c*	9 OMe		199 (1)	201 (6)	169 (2)	73 (47)	
	10 OMe	(x = 0, y = 8)		215 (2)	183 (0.4)	59 (100)	
Δ10*e*	10 OMe	(x = 0, y = 8)	199 (3)	215 (11)	183 (4)	59 (100)	

*C. Application of oxymercuration-demercuration to methyl octadec-*cis*-10-en-5-ynoate [12]*

1. With hydrochloric acid

Reaction of the intermediate mercury compound of methyl octadec-*cis*-10-en-5-ynoate with hydrochloric acid gives methyl 5(6)-ketooctadec-*cis*-10-enoate. Reduction of this unsaturated keto-ester with sodium borohydride furnishes the corresponding methyl 5(6)-hydroxyoctadec-*cis*-10-enoate, which on further treatment with mercuric acetate in methanol followed by demercuration with excess sodium borohydride gives methyl 5-hydroxy, 10(11)-methoxyoctadecanoate and the 2,6-disubstituted tetrahydropyranyl derivative, . Their structures are confirmed by IR, NMR and MS analyses.

2. With sodium borohydride

Reaction of the intermediate mercury compound of methyl octadec-*cis* -10-en-5-ynoate with excess aqueous sodium borohydride solution gives only a mixture of 5(6)-hydroxy, 10(11)-methoxyoctadecanoate isomers. Separation of this mixture into individual components is not possible, but a combination of IR, NMR and MS analyses of their trimethylsilyl derivatives confirm their structures.

III. Experimental

A. Spectroscopic and chromatographic procedures

IR spectra were recorded on a Perkin Elmer 337 grating spectrophotometer using neat liquids sandwiched between 5 mm thick potassium bromide plates.

Mass spectra were recorded on a Hitachi RMS-4 mass spectrometer. Samples were introduced by direct insertion or via a Varian 1868-4 chromatograph. Spectra were normally run at 70 eV with a source pressure of 10^{-6} torr and a temperature of 150–180°C.

Nuclear magnetic resonance spectra were recorded on 15% solutions in deuterated chloroform using a Hitachi Perkin Elmer 20A spectrometer (60 MHz). Chemical shifts were measured in ppm downfield from internal tetramethylsilane ($\tau = 10$).

Analytical TLC was carried out in the usual manner and GLC analyses were performed on a Pye 104 chromatograph and retention values reported as equivalent chain lengths [13].

B. Methoxymercuration-demercuration of methyl cis*-undecenoates*

The following reaction is typical. Excess of mercuric acetate (220 mg, 0.691 mmole) and methyl *cis*-undecenoate (50 mg, 0.255 mmole) in methanol

(10 ml) were left in a stoppered flask for 4 days. The intermediate mercury compound was reduced by the addition of sodium borohydride (48 mg, 1.269 mmole), dissolved in water (10 ml) at 0–5°C. After stirring at room temperature for 2 hr, saturated aqueous sodium chloride solution (50 ml) was added and the reaction mixture extracted with diethyl ether.

The products of each methoxymercuration-demercuration reaction were identified by GLC–MS analysis. GLC, NMR and MS results are recorded in tables 1–3.

C. Oxymercuration-demercuration of methyl 9- and 10-undecynoates with

1. Sodium borohydride

Excess of mercuric acetate (2.55 g, 8.02 mmole and methyl 10-undecynoate (736 mg, 3.755 mmole) in methanol (200 ml) were left in a stoppered flask for 4 days. The oxymercuration product was reduced when excess of sodium borohydride (4.2 g, 0.112 mole), dissolved in water (30 ml), was added dropwise, with stirring at 0–5°C to the oxymercuration reaction mixture. After stirring for 3 hr at room temperature, saturated aqueous solution of sodium chloride (250 ml) was added and the mixture extracted with diethyl ether. Methyl 10-hydroxyundecanoate (460 mg, 58% yield) was isolated by silica column (10 g) chromatography.

A similar reaction was carried out with methyl 9-undecynoate and 9(10-hydroxyundecanoate (96% yield) was obtained.

2. Hydrochloric acid

When a duplicate set of the oxymercuration product of the same alkynoates was treated with hydrochloric acid in methanol (5M, 50 ml) and stirred for 30 min at room temperature, isolation of the products gave the methyl 9(10)- (96%) and 10-keto-ester (94%) for the $\Delta 9a$ and $\Delta 10a$ ester respectively.

D. Oxidation of methyl 9(10)-hydroxyundecanoate

Methyl 9(10)-hydroxyundecanoate (19 mg, 0.089 mmole) in acetone (10 ml) was treated with chromic acid (prepared from 54 mg chromium trioxide, 100 mg concentrated sulpuric acid and made up to 0.5 ml with water, for 15 min at 0–5°C. Water (20 ml) was added and the product was isolated with diethyl ether. GLC analysis of the product showed 46 : 56 ratio of methyl 9-oxo- to 10-oxoundecanoate.

*E. Oxymercuration-demercuration of methyl octadec-*cis*-10-en-5-ynoate with*

1. Sodium borohydride

Excess of mercuric acetate (1.8 g, 5.64 mmole) and methyl octadecenynoate (256 mg, 0.876 mmole) and methanol (80 ml) were left in a stoppered flask for 4 days. Sodium borohydride (2.4 g, 0.063 mole) in water (50 ml) was added dropwise with stirring at 0–5°C to the oxymercurated product and allowed to react for a further 2 hr at room temperature. Saturated aqueous sodium chloride solution (50 ml) was added and the product extracted with diethyl ether. The extract was chromatographed on a silica column (20 g) using n-hexane-diethyl ether mixtures as eluent. Methyl 5(6)-hydroxy, 10(11)-methoxyoctadecanoate (143 mg, 48%) was isolated.

2. Hydrochloric acid

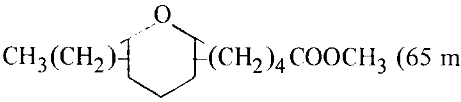
The oxymercuration reaction was repeated with methyl octadecenynoate (1 g), mercuric acetate (7.6 g, 0.024 mole) and methanol (200 ml). Excess hydrochloric acid in methanol (5M, 200 ml) was added to the oxymercurated product and stirred for $\frac{1}{2}$ hour at room temperature. The product was isolated in the usual manner and purification on a silica (20 g) chromatographic column gave methyl 5(6)-oxooctadec-*cis*-10-enoate (470 mg, 44.8%).

*F. Reduction of methyl 5(6)-oxooctadec-*cis*-10-enoate*

Sodium borohydride (750 mg, 19.84 mmole) in water (10 ml) was added to methyl 5(6)-oxooctadec-*cis*-10-enoate (300 mg, 0.967 mmole) in methanol (50 ml) and stirred at room temperature for 1 hr. Extraction with diethyl ether gave methyl 5(6)-hydroxyoctadec-*cis*-10-enoate (297 mg, 99%).

*G. Oxymercuration-demercuration of methyl 5(6)-hydroxyoctadec-*cis*-10-enoate*

A mixture of methyl 5(6)-hydroxyoctadec-*cis*-10-enoate (200 mg, 0.634 mmole) in methanol (30 ml) and mercuric acetate (800 mg, 2.51 mmole) was left in a stoppered flask for 4 days. Excess of sodium borohydride (500 mg, 13.33 mmole) in water (30 ml) was added to the oxymercurated compound at 0–5°C and stirred for 2 hr at room temperature. The product was extracted and isolation of the components by silica column (20 g) chromatography gave methyl 5-hydroxy-10(11)-methoxyoctadecanoate (16 mg) and the tetrahydropyranyl derivative,



(65 mg).

GLC, NMR and MS results of the isolated products (and their trimethylsilyl derivatives) are given in the Appendix.

Appendix

MS, NMR, IR and GLC results of various oxymercuration-demercuration products.

Values quoted are *m/e*, origin of fragment, and intensity relative to the base peak = 100. Peaks are quoted in decreasing value of *m/e* except for mixtures where the fragments are separated into groups relating to each component of the mixture. Those marked with an asterisk may result from more than one component of the mixture.

Chemical shifts are measured in ppm downfield from internal tetramethylsilane ($\tau = 10$).

ECL (equivalent chain lengths) values are calculated with reference to saturated methyl esters on Silar 10C stationary phase.

A. Methyl hydroxyundecanoates

(i) Methyl 9(10)-hydroxyundecanoate:

NMR signals: 9.08 ($C\underline{H}_3CH_2$–), 8.83 (doublet, $C\underline{H}_3CHOH$–)
8.5–8.75 (–$(C\underline{H}_2)_n$–), 7.7 (–$C\underline{H}_2COOMe$)
and 6.35 τ (4H, –$COOC\underline{H}_3$ and $CH_3C\underline{H}OH$–).

IR: 3400 (O–H stretching) and 1740 cm^{-1} (ester carbonyl stretching).

ECL: 25.2 (broad peak with tailing).

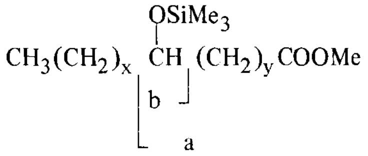
(ii) Methyl 10-hydroxyundecanoate:

NMR signals: 8.84 (doublet, $C\underline{H}_3CHOH$–),
8.5–8.7 (–$(C\underline{H}_2)_n$–), 7.7
(–$C\underline{H}_2COOMe$) and 6.34 τ
(4H, –$COOC\underline{H}_3$ and $CH_3C\underline{H}OH$–).

IR: 3450 (O–H stretching) and 1745 cm^{-1} (ester carbonyl stretching).

ECL: 24.4 (broad peak with tailing).

B. Methyl trimethylsilyloxyundecanoates



$$CH_3(CH_2)_x\,\underbrace{\overset{OSiMe_3}{\underbrace{\overset{|}{CH}}_{b}}\,(CH_2)_y}_{a}COOMe$$

(i) Methyl 9(10)-trimethylsilyloxyundecanoate:

MS major peaks:

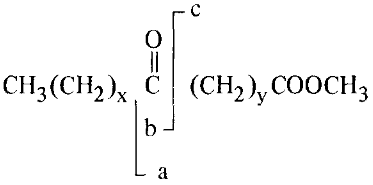
288 (M, 1)*	273 (M–15, 34)*	259 (a, 92)
257 (M–31, 23)*	230 ($\cdot(CH_2)_7\underset{\substack{\| \\ +OSiMe_3}}{C}OMe$, 23)	131 (b, 51)
288 (M, 1)*	273 (a, 34)*	257 (M–31, 23)*
244 ($\cdot(CH_2)_8\underset{\substack{\| \\ +OSiMe_3}}{C}OMe$, 40)	117 (b, 100)	

(ii) Methyl 10-trimethylsilyloxyundecanoate:

MS major peaks:

288 (M, 1)	273 (a or M–15, 40)	257 (M–31, 16)
244 ($\cdot(CH_2)_8\underset{\overset{\|}{+OSiMe_3}}{C}OMe$, 63)	117 (b, 100)	73 ($^+SiMe_3$, 78)

C. Methyl oxoundecanoate



$CH_3(CH_2)_x\overset{O}{\overset{\|}{C}}(CH_2)_yCOOCH_3$

(i) Methyl 9(10)-oxoundecanoate:

NMR signals: 8.71 ($C\underline{H}_3CH_2CO$–), 8.91 (–$(CH_2)_n$–),
8.4 (–$C\underline{H}_2CH_2CO$–), 7.9 ($C\underline{H}_3CO$–),
7.72 (–$C\underline{H}_2CO$–) and 6.35 τ (–$COOC\underline{H}_3$).

IR: 1740 (ester carbonyl stretching) and
1720 cm^{-1} (oxo carbonyl stretching).

ECL: 20.25 (9-oxo-) and 20.74 (10-oxo-).

MS major peaks:

(x = 1, y = 7)

214 (M, 20)*	199 (M–15, 5)*	183 (M–31, 71)*
185 (a, 62)	157 (c, 89)*	154 (a–31, 13)
142 (c–15, 27)	143 (c–14, 87)	111 (c–15–31, 61)
72 (b + 15, 84)	71 (b + 14, 40)	57 (b, 61)*

(x = 0, y = 8)

214 (M, 20)*	199 (a or M–15, 5)*	183 (M–31, 71)*
171 (c, 1)	168 (a–31, 37)	157 (c–14, 89)*
156 (c–15, 23)	125 (c–15–31, 56)	58 (b + 15, 26)
57 (b + 14, 61)*	43 (b, 100).	

(ii) Methyl 10-oxoundecanoate:

NMR signals: 8.71 (–$(CH_2)_n$–), 8.4 (–$C\underline{H}_2CH_2CO$–)
7.9 ($C\underline{H}_3CO$–), 7.72 (~4H, –$C\underline{H}_2CO$–)
and 6.35 τ (–$COOC\underline{H}_3$).

IR: 1740 (ester carbonyl stretching) and
1715 cm^{-1} (oxo carbonyl stretching).

ECL: 20.74

MS major peaks:

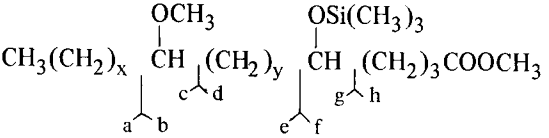
(x = 0, y = 8)

214 (M, 15)	199 (a or M--15, 7)	183 (M–31, 51)
171 (c, 5)	168 (M–31, 1)	157 (c–14, 100)
156 (c–15, 35)	125 (c–14–32, 45)	58 (b + 15, 63)
57 (b + 14, 13)	43 (b, 74)	

D. Methyl hydroxy, methoxyoctadecanoates

(i) Methyl 5(6)-hydroxy, 10(11)-methoxyoctadecanoate:
NMR signals: 9.12 ($C\underline{H}_3CH_2$–), 8.5–8.8 (–$(C\underline{H}_2)_n$–),
7.7 (–$C\underline{H}_2$COOMe), 6.7 (–CH–$OC\underline{H}_3$),
6.55 (–$C\underline{H}$OH) and 6.35 τ (–$COOC\underline{H}_3$).
IR: 3475 (O–H stretching) and 1740 cm^{-1} (ester carbonyl stretching).

(ii) Methyl 5-trimethylsilyloxy, 10(11)-methoxyoctadecanoate:



$$CH_3(CH_2)_x\overset{OCH_3}{CH}(CH_2)_y\overset{OSi(CH_3)_3}{CH}(CH_2)_3COOCH_3$$

MS major peaks:

(x = 7, y = 4)

416 (M, 3)*	401 (M–15, 9)*	385 (M–31, 6)*
315 (g, 100)*	303 (b, 44)	259 (d, 3)
213 (e, 17)*	203 (f, 93)*	157 (c, 42)
113 (a, 21)	101 (h, 9)*	

(x = 6, y = 5)

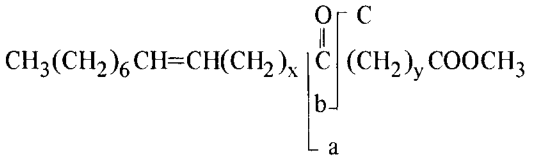
416 (M, 3)*	401 (M–15, 9)*	385 (M–31, 6)*
317 (b, 31)	315 (g, 100)*	273 (d, 2)
213 (e, 17)*	203 (f, 93)*	143 (c, 59)
101 (h, 9)*	99 (a, 25).	

E. Methyl 5(6)-oxooctadec-cis-10-enoate:

NMR signals: 9.12 ($C\underline{H}_3CH_2$–), 8.72 (–$(C\underline{H}_2)_n$–),
8.4 (–$C\underline{H}_2CH_2$COOMe), 8.03 (–$C\underline{H}_2$CH=CH$C\underline{H}_2$–),
7.5–7.8 (6H, –$C\underline{H}_2$COOMe and –$C\underline{H}_2COC\underline{H}_2$–),
6.35 (–$COOC\underline{H}_3$) and 4.66 τ (triplet, –C$\underline{H}$=C$\underline{H}$–).

ECL: 26.6

IR: 1740 (ester carbonyl stretching) and 1700 cm^{-1}
(oxo carbonyl stretching).

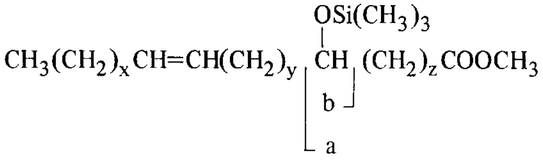


$$\mathrm{CH_3(CH_2)_6CH{=}CH(CH_2)_x\overset{O}{\overset{\|}{C}}(CH_2)_yCOOCH_3}$$

MS major peaks:
(x = 4, y = 3)
310 (M, 8)*
279 (M–31, 11)*
223 (b + 14, 20)
224 (b + 15, 2)
210 (b + 1, 3)
209 (b, 11)*
166 (M–a–15, 4)
144 (a + 15, 100)*
143 (a + 14, 80)
130 (a + 1, 14)
129 (a, 63)
113 (a + 15–31, 53)
101 (c, 64)
86 (c–15, 5)
55 (c–15–31, 82)

(x = 3, y = 4)
310 (M, 8)*
279 (M–31, 11)*
210 (b + 15, 4)
209 (b + 14, 11)*
196 (b + 1, 11)
195 (b, 3)
158 (a + 15, 57)
157 (a + 14, 34)
152 (M–a–15, 7)
144 (a + 1, 100)*
143 (a, 80)
115 (c, 11)
127 (a + 15–31, 21)
100 (c–15, 6).

F. Methyl 5(6)-trimethylsilyloxyoctadec-cis-10-enoate:



$$\mathrm{CH_3(CH_2)_xCH{=}CH(CH_2)_y\overset{OSi(CH_3)_3}{\overset{|}{CH}}(CH_2)_zCOOCH_3}$$

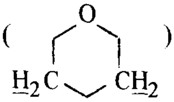
MS major peaks:
(x = 6, y = 4 and z = 3)
384 (M, 9)*
369 (M–15, 54)*
353 (M–31, 15)*
337 (M–47, 12)*
294 (M–90, 69)*
283 (b, 40)
203 (a, 58)
73 ($^+$SiMe$_3$, 100)*

(x = 6, y = 3 and z = 4)
384 (M, 9)
369 (M–15, 54)*
353 (M–31, 15)*
337 (M–47, 12)*
294 (M–90, 69)*
269 (b, 29)
217 (a, 61)
73 ($^+$SiMe$_3$, 100)*

G. Methyl 6, 10-epoxyoctadecanoate:

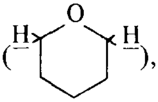
NMR signals: 9.11 ($C\underline{H}_3CH_2$–), 8.71 (–$(CH_2)_n$–),

8.53 (



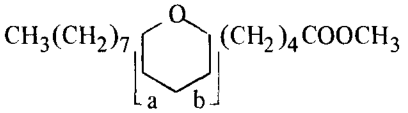
), 8.35 (–$C\underline{H}_2CH_2COOMe$),

7.7 (–$C\underline{H}_2COOMe$), 6.8 (



),

and 6.35 τ (–$COOC\underline{H}_3$).



MS major peaks:

313 (M + 1, 31)	312 (M, 24)	311 (M–1, 4.5)
294 (M–18, 3)	281 (M–31, 7)	263 (M–49, 19)
200 (a + 1, 31)	199 (a, 37)	198 (b + 1, 31)
197 (b, 66)	181 (a–18, 47)	179 (b–18, 100)
167 a–32, 50)	149 (a–50, 82).	

References

[1] K.A. Hofmann and J. Sand, Chem. Ber. (1900) 1340

[2] J. Chatt, Chem. Rev. 48 (1951) 7;
W. Kitching, Organometal. Chem. Rev. 3 (1968) 61;
H.C. Brown and J.T. Kurek, J. Am. Chem. Soc. 91 (1969) 5647;
P. Abley, F.J. McQuillin, D.E. Minikin, K. Kusamran, K. Maskens and N. Polgar, Chem. Commun. (1970) 348;
G.M. Whitesides and J. San Filippo, Jr., J. Am. Chem. Soc. 92 (1970) 6611;
A. Lethbridge, R.O.C. Norman and C.B. Thomas, J. Chem. Soc., Perkin Trans. 1 (1974) 1929;
D.S. Matteson, Organometallic Reaction Mechanisms. Academic Press, New York (1974) 202;
R.D. Bach and R.N. Brummel, J. Am. Chem. Soc. 97 (1975) 453

[3] G.A. Olah and P.R. Clifford, J. Am. Chem. Soc. 95 (1973) 6067

[4] N.A. Bell and S.W. Breuer, J. Chem. Soc., Perkin Trans. 2 (1974) 717

[5] F.D. Gunstone and R.P. Inglis, Chem. Phys. Lipids 10 (1973) 73, 89, 105

[6] D.E. Minnikin, P. Abley, F.J. McQuillin, K. Kusamran, K. Maskens and N. Polgar, Lipids 9 (1974) 135

[7] E. Jantzen and H. Andreas, Chem. Ber. 92 (1959) 1427;
E.M. Stearns, Jr., H.B. White, Jr. and F.W. Quackenbush, J. Am. Oil Chem. Soc. 39 (1962) 61;
H.B. White, Jr. and F.W. Quackenbush, ibid. 39 (1962) 511;
S.P. Fore, F.G. Dollear and G. Sumrell, Lipids 1 (1966) 73;

H.B. White, Jr. J. Chromatog. 21 (1966) 213
[8] A.E. Borisov, V.D. Vilchevskaya and A.N. Nesmeyanov, Proc. Acad. Sci. USSR 90 (1953) 383, Chem. Abstr. 48 (1954) 4434g; Bull. Acad. Sci. USSR Div. Chem. Sci. (1954) 879, Chem. Abstr. 50 (1956) 5509f
[9] P.F. Hudrlik and A.M. Hudrlik, J. Org. Chem. 38 (1973) 4254
[10] A. Seher, Archiv, Pharm. 292 (1959) 519
[11] M.S.F. Lie Ken Jie and C.H. Lam, J. Chromatog. 97 (1974) 165
[12] M.S.F. Lie Ken Jie and G. Tsang, Chem. Phys. Lipids 13 (1974) 21
[13] T.K. Miwa, K.L. Mikolajczak, F.R. Earle and I.A. Wolff, Anal. Chem. 32 (1960) 1739