Pergamon

Tetrahedron, Vol. 53, No. 31, pp. 10883-10898, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00694-7

Dienediolates of Unsaturated Carboxylic Acids in Synthesis. Aldehydes and Ketones from Alkyl Halides, by Ozonolysis of β,γ-Unsaturated α-Alkyl Carboxylic Acids. The Role of a Tertiary Amine in the Cleavage of Ozonides.

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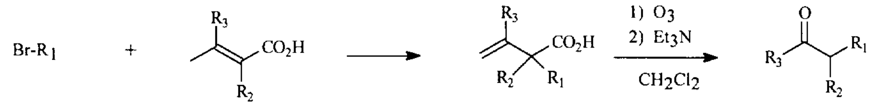
Abstract: A convenient two-step procedure for a two carbon homologative conversion of alkyl halides into aldehydes and methyl ketones by α-alkylation of unsaturated carboxylic acids, followed by ozonolysis is developed and applied to the synthesis of ω-chloro aldehydes. Triethylamine is superior to dimethyl sulfide or triphenylphosphine for cleavage of the ozonides, except when aldol condensation side reactions require use of protic solvents and iodide salts. Cleavage of the ozonides by triethylamine is shown to occur mainly through a reductive process. © 1997 Elsevier Science Ltd.

During our studies on the synthesis and slow delivery of pheromones, [1-4] we were interested in the preparation of unbranched ω-halogeno aldehydes. The commercially available acetals of the two and three carbon atom halogeno aldehydes are widely used, but for the synthesis of pheromones higher homologs are required. These valuable synthetic building blocks are commonly prepared by methods which do not differ substantially from the general procedures used for other aldehydes; namely reduction of their corresponding carboxylic acids, [5] acyl chlorides, [6,7] or nitriles, [8,9] oxidation of the halogeno alcohols, [10] alkylation of the cyclohexylimine of acetaldehyde, [11] or copper catalyzed Grignard coupling of a lower homolog with a 1-bromo-ω-chloroalkane. [12] More specific methods are based on cleavage of cyclic ethers or lactones with hydrogen halides, followed by oxidation or reduction of intermediate alcohols or esters. [13,14] Other methods start by ozonation of cycloalkenes, [2, 15] or by oxidative cleavage of cycloalkanols with lead tetraacetate. [16]

Selective alkylation of the lithium dianion of 2-butenoic acid with α,ω-alkyl dihalides may give 2-alkyl 3-butenoic acids. Ozonolysis of these should lead to β-aldo carboxylic acids, which on decarboxylation would provide an easy route to the ω-halogeno aldehydes. [17] As a whole, the two step sequence would become equivalent to the use of butenoic acid as an acetaldehyde enolate synthon (Scheme 1).

Although the study was aimed at the preparation of unbranched ω-halogeno aldehydes, its scope was extended to a few alkyl halides and to the preparation of other ω-halogeno carbonylic compounds, namely α-methyl aldehydes, and 2-ketones by use of 2-methyl-2-butenoic and 3-methyl-butenoic acids **3** and **4** in order to show the wider applicability of the method. With the same consideration as before, the latter acids could become convenient synthons for propanal and acetone, respectively. ω-Halogeno 2-ketones have been prepared by cleavage of tertiary cycloalkanols or acyllactones, [18] by application of general methods, such as the well known alkylation of ethyl acetoacetate, [19] free ketones, imines or hydrazones, [20] or by conjugate additions to unsaturated ketones. [21] On the contrary, few references are found in the Literature for α-methyl ω-halogeno aldehydes. [8, 14] In the course of the present work triethylamine has proved a convenient reagent for cleavage of the ozonides, and some experiments have now been carried out in order to find out to what extent a basic catalyzed decomposition [22, 23] or a reductive process, [24] are operative.



1a; R_1 = $(CH_2)_3Cl$
1b; R_1 = $(CH_2)_4Cl$
1c; R_1 = $(CH_2)_5Cl$
1d; R_1 = $(CH_2)_9CH_3$
1e; R_1 = $(CH_2)_{11}CH_3$
1f; R_1 = CH_2Ph

2; R_2 = R_3 = H
3; R_2 = Me; R_3 = H
4; R_2 = H; R_3 = Me

5; R_2 = R_3 = H
6; R_2 = Me; R_3 = H
7; R_2 = H; R_3 = Me

8; R_2 = R_3 = H
9; R_2 = Me; R_3 = H
10; R_2 = H; R_3 = Me

Scheme 1

Alkylation of 2-butenoic acids **2** to **4** with α,ω-bromochloroalkanes **1a** to **1c** and of acid **2** with 1-bromoalkanes **1d** to **1f** led to the 2-substituted-3-butenoic acids **5** to **7**. Although the regioselectivity of the alkylation is high in every case, α,α-dialkylation, could not be completely avoided for alkylation of 2-butenoic acid **2**. This double alkylation was accompanied by oligomerization for α,ω-dibromo- α,ω-bromochloro-alkanes as alkylating agents. Pure 2-substituted 3-butenoic acids **5** were obtained in 54 to 68 % yields after bulb to bulb distillation. Spectroscopically pure (^1H and ^{13}C NMR) acids **6** and **7** were obtained directly in 83 to 96 % yields.

Ozonations were usually carried out at -70° in dichloromethane. Triethylamine, triphenylphosphine and the widely recommended dimethyl sulfide were used for cleavage of the ozonides. For the latter reagent, better results were obtained when ozonation was carried out in the presence of pyridine. [25] Methanol as solvent, and potassium iodide for reduction of the resulting ozonized material were used later on in order to avoid side aldol condensations (see below).

Ozonolysis of the 2-methyl substituted chloroalkyl acids **6** gave good yields of spectroscopically pure (^{1}H NMR and ^{13}C NMR) 2-methyl-ω-chloroaldehydes **9** when cleavage of the ozonide was carried out with triethylamine. In agreement with Hon's findings, [23] this cleavage agent was superior to dimethyl sulfide and to triphenylphosphine, as shown in Table 1 . With the latter reagents cleavage occurred much more slowly, and isolation and purification by bulb to bulb distillation or column chromatography was required.

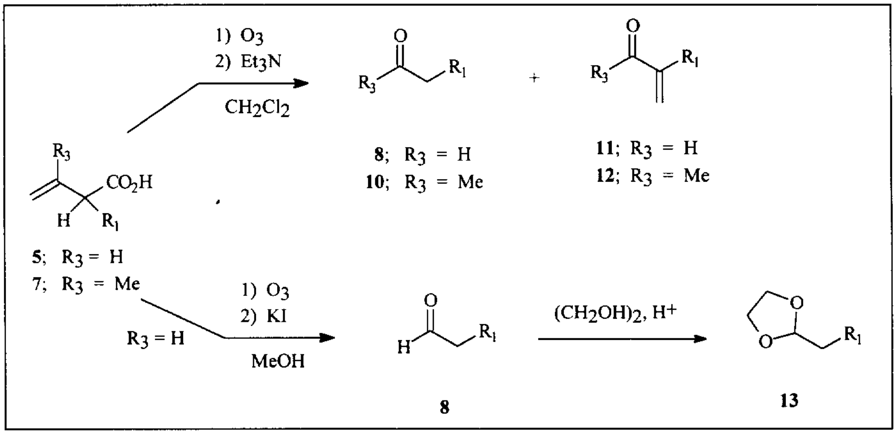
Table 1. Ozonation of Unsaturated acids **6** to α-Methyl-ω-chloro aldehydes **9**

Chloro Acid	Reducing Agent	Time (h)	Yield (%)
6a	Et_3N	1	71^a
	Me_2S	15	27^b
6b	Et_3N	1	73^a
	Me_2S	15	50^c
	Ph_3P	15	60^c
6c	Et_3N	1	77^a
	Me_2S	15	40^c

a.- Isolated as spectroscopically pure material (^{1}H and ^{1}3C NMR); b.- Purified by bulb to bulb distillation; c.- Purified by column chromatography.

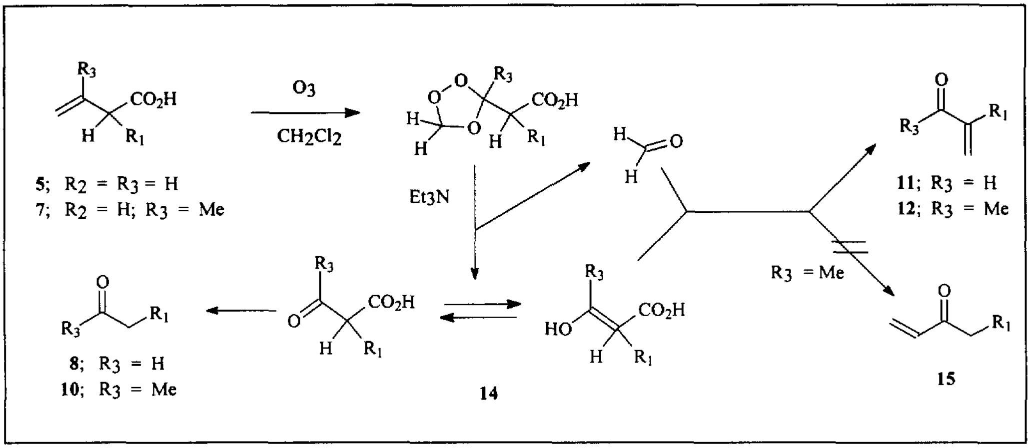
Chloroalkyl acids **5** and **7** were more complex in their ozonolyses, as the expected aldehydes **8** and methyl ketones **10** were accompanied by significant amounts of the corresponding methylene compounds **11** and **12** (Scheme 2). These aldol condensation products were not isolated, except for the ketone **12a.** Analyses by GLC of the mixtures revealed the presence of two components, and molecular mass values obtained by GLC-MS were in agreement with those expected for the aldehydes **8a** to **8c** and **11a** to **11c**. For acids **5** as starting materials, the ^{1}H NMR spectra of the mixtures of ozonolytic products showed a triplet (J 1.2 Hz) at 9.74 ppm and a singlet at 9.50 ppm, indicative of two aldehydes being present, as well as two singlets at 6.06 and 6.32, due to the aldehydes **11**. Similarly, in the spectra of the mixtures resulting from ozonolysis of acids **7a** and **7b** two singlets at 5.84 and 6.06 were observed for the methylene ketone **12a** and at 5.76 and 6.06 for its homolog **12b**. Although the methylene aldehydes **11** were found regardless of the reagent used for cleavage of the ozonide (see Table 2), the methylene ketones **12** were observed only for triethylamine. Thus, cleavage of the ozonides derived from acids **7a** and **7b** with this amine led to 40:60 and 58:40 mixtures of the corresponding ketones **10** and **12**, respectively. From the first mixture methylene ketone **12a** was isolated in 38 % yield.

As the methylene aldehydes were found regardless of the nature of the cleavage reagent, formaldehyde must be removed from the reaction solution in order to obtain a single aldehyde. This was achieved by use of methanol as solvent. Satisfactory results for chloro aldehydes **8** were obtained when the ozonation was carried out in methanol, and the reduction of the intermediate hydroperoxides was carried out with aqueous potassium iodide (Scheme 2). [26] Although aldehydes thus obtained were spectroscopically pure, chloro aldehydes and long chain aldehydes thus obtained proved unstable on standing, or on purification by either bulb to bulb distillation or column chromatography, when they apparently led to oligomerization products. On these occasions acetalization with ethylene glycol under conventional conditions gave the corresponding dioxolanes **13**, and these could be purified conveniently.



Scheme 2

The side aldol condensations are the only significant anomalous behaviour in these ozonolyses, and they most probably require the presence of the carboxyl group. Indeed, no aldol condensation was observed now when formaldehyde generated from paraformaldehyde [27] was collected in dichloromethane and immediately allowed to react with decanal in the presence of triethylamine. Besides, only 3-methylene 2-alkanones **12** are obtained, instead of the 1-alkene-2-ones **15**, which should be expected from a base catalyzed aldol condensation of the methyl ketones **10** with formaldehyde. The addition to formaldehyde probably occurs through the enol form of the β-carboxylic aldehyde or ketone **14** (Scheme 3), and followed by decarboxylative dehydration, as the intermediate hydroxy aldehydes or hydroxy ketones have not been observed in any occasion. Thus in one experiment, ozonation of acid **5a** was carried out in dichloromethane under the usual conditions at -70° C, the solution was flushed with argon for 10 min at the same temperature, triethylamine was added to the reaction solution at -70° C, and this was allowed to warm up to room temperature. Two aliquot samples were taken before the addition of the amine, and a third one before work-up. The ^{1}H NMR spectrum of the first one of the samples was carried out in the same reaction solvent, and revealed the presence of only very tiny amounts of any aldehyde in the solution, thus showing that no formaldehyde was practically present.The signals of the ozonide at 5-6 ppm were blurred by the signal of the solvent, but the peaks of the



Scheme 3

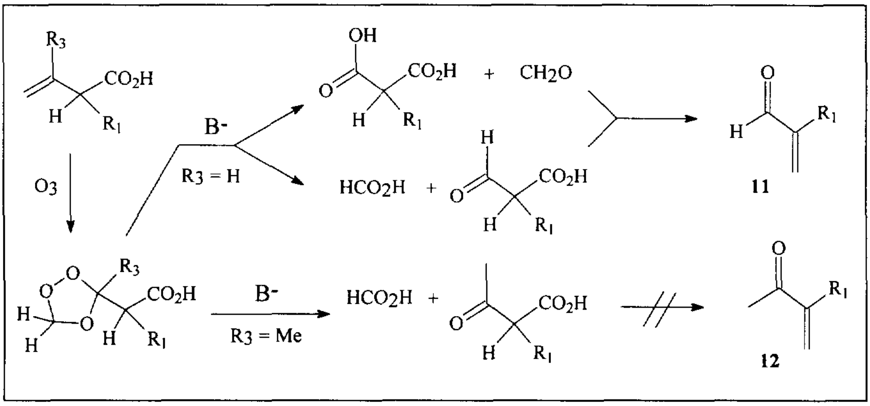
Table 2. Ozonation of Unsaturated Carboxylic Acids **5** and **7**

Starting Acid	Cleavage Reagent	Time (h)	**8/11** Ratio	**8/11** Yield (%)^a	**10** Yield (%)^a	**13** Yield (%)^a
5a	Me$_2$S^b	15	58/42	55		
	Et$_3$N	1	70/30	73		
	Ph$_3$P	15	70/30	(73)		
	KI^c	1	100/0	91		98 (80)
5b	Me$_2$S^b	15	72/28	62 (38)		
	KI^c	1	100/0	84		94 (77.5)
5c	Me$_2$S^b	15	66/33	(31)		
	KI^c	1	100/0	83^d		83 (74.5)^c
5d	KI^c	1	100/0	83^d		
5e	KI^c	1	100/0	92^d		96 (66)
5f	KI^c	1	100/0	90 (77)		
7a	Me$_2$S^b	15			(51)	
7b	Me$_2$S^b	15			(58)	
	PPh$_3$	15			(32)	
7c	Me$_2$S^b	15			(63)	

a.- In brackets, yield for bulb to bulb distilled material; b.- Ozonation carried out with a catalytic amount of pyridine; c.- Ozonation carried out in methanol; d.- Isolated as spectroscopically pure material (^{1}H and ^{13}C NMR).

chloroalkyl chain were observed as normal. When the solvent of the second aliquot was evaporated, and the residue dissolved in CDCl$_3$, the spectrum showed the complex pattern at 5-6 ppm expected for the ozonide,[23] along with the signals for the chloroalkyl chain. The solvent of the third aliquot was evaporated, and the residue dissolved in CDCl$_3$. The ^{1}H NMR spectrum of this solution showed the presence of both aldehydes **8a** and **11a** in a nearly 4:3 ratio, through the signals referred to above. Also, the spectrum showed a singlet at 8.54 ppm, which might be due to formic acid, and a quadruplet at 2.98 and a triplet at 1.22, probably due to triethylamine N-oxide (see below). When the reacting mixture was subject to the usual work-up, only a 4:3 mixture of aldehydes **8a** and **11a** was found (^{1} HNMR). According to this experiment both generation of formaldehyde and its condensation occurred during treatment of the ozonide with triethylamine.

The presence of the methylene aldehydes and ketones and the observations of the latter experiment were not expected in view of the reports on the base-catalyzed decomposition of ozonides by tertiary amines, as this leads to aldehydes/or ketones and to carboxylic acids whenever structurally feasible. [22] Ozonolysis of cycloalkenes with cleavage by triethylamine neatly affording ω-oxo-carboxylic acids or their derivatives have been recently described by Hon and by Wu. [23, 28] However, Razumovskii has shown that tertiary amines cleave ozonides through a reductive process. [24] In the present study, treatment of the ozonides with triethylamine or with dimethyl sulfide gave the aforementioned aldehydes and ketones, along with only minor amounts of complex mixtures of carboxylic acids. The ^{1}H NMR spectra of these mixtures derived from acids **5** revealed the presence of small amounts of the expected malonic acids through a triplet at 3.35 ppm, and monocarboxylic acids might be present as well, as another triplet is generally observed at 2.25 ppm. Furthermore, the presence of the methylene aldehydes **11** in the reaction mixtures suggest a reductive mechanism, and the high ratios observed for methylene ketones **12** (see above) cannot be the result of a predominant basic cleavage of the ozonides, as this would generate only minor amounts of formaldehyde, and hence only tiny amounts of methylene ketones **12** would result (Scheme 4).



Scheme 4

One experiment was carried out in order to find out whether in the present case ozonides are cleaved by the amine through a reductive process. It is known that amine oxides are the main products of the reaction of tertiary amines with ozone. [29, 30] When dichloromethane was saturated with ozone at -70°C, and triethylamine was added to the solution, a crude material was obtained on evaporation of the solvent, whose ^{1}H NMR spectrum showed, as main signals, a quadruplet at 2.98 ppm and a triplet at 1.22 ppm, in good agreement with the chemical shifts described for the N-oxide of triethylamine, although the compound was not isolated. [31] The same spectrum was observed afterwards when cleavage of the ozonide of acid **5a** was carried out with triethylamine, which had been added only after thorough evaporation of the solvent, and solution of the residue in fresh dichloromethane, in order to make sure that no ozone was present in the reaction mixture.

In conclusion, we have developed a convenient two-step procedure for a two carbon homologative conversion of alkyl halides into aldehydes and methyl ketones, which has been applied to the preparation of ω-halogeno aldehydes and ketones. Triethylamine is here superior to dimethyl sulfide or triphenylphosphine for cleavage of the ozonides derived from β,γ unsaturated carboxylic acids, except when aldol condensation side reactions require use of protic solvents and iodide salts. It has also been shown that cleavage of the present intermediate ozonides by triethylamine occurs predominantly through a reductive process.

EXPERIMENTAL PART

IR spectroscopic data were obtained for liquid film or KBr discs, with Bio Rad FTS-7 or Perkin-Elmer 281 spectrophotometers. ^{1}H and ^{13}C NMR spectra were recorded for $CDCl_3$ solutions, with Bruker AC-200 (200 MHz) or 300 Varian Unity (300 MHz) spectrometers, using TMS as internal standard. Mass spectra were determined with a VG Autospec or a Trio 1000 Spectrometers. Elemental analyses were determined by "Centro de Investigación y Desarrollo (CSIC) de Barcelona. Melting points are uncorrected and were measured with a Reichert apparatus. Bulb to bulb distillations were carried out with a Büchi GKR-50 apparatus; Boiling point temperatures stand for temperature of the furnace. Silica gel Merck 60 (0.06-0.20 mm) was used for column chromatography, and silica gel Merck 60 (230-400 mesh) for flash column chromatography, in any case with elution with hexane/ether mixtures. Tetrahydrofuran (THF) was distilled from blue sodium diphenylketyl immediately before use. Dichloromethane was washed with conc sulfuric acid, dried, and distilled. [32] Diethylamine was dried over CaH_2 and distilled before use. Lithium diethylamide (LDE) has been generated from lithium, naphthalene, and diethylamine, as previously described. [33] Generation and reactions of the dienediolates of carboxylic acids were carried out under argon atmosphere, using standard conditions for exclusion of moisture. The reaction temperature (-70°C) was achieved by cooling with a CO_2/acetone bath. Evaporation of solvents was carried out with a vacuum rotatory evaporator and a bath at 40°C.

General procedure for reaction of carboxylic acids 2 to 4 with alkyl bromides. The carboxylic acid (9 mmol) in THF (20 ml for 2-butenoic acid **2**, and 10 ml for 2- and 3-methyl-2-butenoic acids **3** and **4**) was added dropwise for 30 min to lithium diethylamide [from lithium (20 mmol), naphthalene (1.28 g) and diethylamine (2.1 ml)] in THF (20 ml for acid **2**, and 10 ml for acids **3** and **4**) at -70°C. The solution was stirred for 1h at the same temperature for the acids **2** and **4** or for 5 min at the same temperature, and then allowed to warm to 0°C for 1 h, and cooled again at -70°C for the acid **3**. The alkyl bromide **1** (9 mmol) in THF (20 ml for acid **2** and 10 ml for acids **3** and **4**) was added dropwise over 20 min, and the mixture stirred at the same temperature for another 30 min. The cooling bath was then removed, and the solution stirred for 1h at 0°C. Water (30 ml) was added, the solvent was partly evaporated under reduced pressure, and the residue extracted with ether. The aqueous layer was acidified, under stirring and ice-water cooling by slow addition of conc hydrochloric acid, extracted with ethyl acetate and the organic layer dried. Evaporation of the solvent gave crude acids **5** to **7**, which were purified by bulb to bulb distillation, unless spectroscopically pure (^{1}H NMR, ^{13}C NMR).

5-Chloro-2-ethenylpentanoic acid 5a.- According to the general method, 2-butenoic acid **2** (1.55g; 18 mmol), and 1-chloro-3-bromopropane **1a** (2.87 g; 18 mmol) gave a yellow oil (2.57 g; 88 %) which was distilled to give the title compound **5a** as a colourless oil (1.77 g, 60.5 %), bp $_{2\ mm}$ 72° C. Found: C, 51.46; H, 7.00; Cl, 21.51. $C_7H_{11}ClO_2$ requires C, 51.70 ; H, 6.82 ; Cl, 21.80 %; ν_{max} 3700-2400 (OH), 1700 (C=O), 1646 (C=C), and 990 and 928 ($CH=CH_2$) cm^{-1}; δ_H 10.2 (1H, s, CO_2H), 5.77 (1 H, ddd, J 17, 10 and 8.7 Hz, $\underline{CH}=CH_2$), 5.17 and 5.18 (2 H, 2×d, J 17 and 11 Hz, $CH=\underline{CH_2}$), 3.53 (2 H, t, J 6.6 Hz, CH_2Cl), 3.01 (1 H, dt, J 8 and 6.6 Hz, $\underline{CH}CO_2H$), 1.89-1.65 (4 H, m, 2 x CH_2) ppm; δ^{13}C 180.25 (CO_2H), 134.7 ($\underline{C}H=CH_2$), 118.4 ($CH=\underline{C}H_2$), 49.3 ($\underline{C}CO_2H$), 44.38 (CH_2Cl) , and 29.87 and 29.00 (2 x CH_2) ppm.

6-Chloro-2-ethenylhexanoic acid 5b.- Similarly, 2-butenoic acid **2** (1.55 g; 18 mmol), and 1-chloro-4-bromobutane **1b** (3.1 g,18 mmol), after usual work-up, gave a yellow oil (2.8 g; 88 %), which on bulb to bulb distillation gave a colourless oil of the title acid **5b** (2.18 g, 68.5%), bp $_{2\ mm}$ 80° C. Found: (MS, CI+): $(M+1)^+$ 177.067795. $C_8H_{14}ClO_2$ requires 177.068233; ν_{max} 3500-2500 (OH), 1707 (C=O), 1646 (C=C), and 990 and 928 ($CH=CH_2$) cm^{-1}; δ_H 11.0 (1H, s, CO_2H), 5.74 (1 H, ddd, J 17, 9 and 8.4 Hz, $\underline{CH}=CH_2$), 5.17 (2H, 2×d, J 17 and 10 Hz, $CH=\underline{CH_2}$), 3.5 (2 H, t, J 6.5 Hz, CH_2Cl), 3.01 (1 H, dt, J 8 and 6.6 Hz, $\underline{CH}CO_2H$), 1.84-1.43 (6 H, m, 3 × CH_2) ppm; δ^{13}C 180.49 (CO_2H), 135 ($\underline{C}H=CH_2$), 118.1 ($CH=\underline{C}H_2$), 49.89 ($\underline{C}CO_2H$), 44.61 (CH_2Cl) , and 32.19, 31.05 and 24.28 (3 × CH_2) ppm.

7-Chloro-2-ethenylheptanoic acid 5c.- 2-Butenoic acid **2** (1.5489 g; 18 mmol), and 1-chloro-5-bromohexane **1c** (3.3 g, 18 mmol), afforded a yellow oil (2.95 g; 85.5 %) which on bulb to bulb distillation gave the title acid as a colourless oil (2.1 g, 61%), bp $_{1.5\ mm}$ 92° C. Found: (MS, CI+): $(M+1)^+$ 191.083324. $C_9H_{16}ClO_2$ requires 191.083883; ν_{max} 3500-2500 (OH), 1706 (C=O), 1646 (C=C), and 990 and 926 ($CH=CH_2$) cm^{-1}; δ_H 11.0 (1H, s, CO_2H), 5.79 (1 H, ddd, J 18, 9 and 8.8 Hz, $\underline{CH}=CH_2$), 5.16 (2 H , 2×d, J 17 and 11 Hz, $CH=\underline{CH_2}$), 3.5 (2 H, t, J 6.6 Hz, CH_2Cl), and 3.01 (1 H, dt, J 8 and 6.6 Hz, $\underline{CH}CO_2H$), 1.8-1.3 (8

H, m, 4×CH_2) ppm; δ^{13}C 180.63 (CO_2H), 135.27 ($\underline{C}H=CH_2$), 117.89 ($CH=\underline{C}H_2$), 49.98 ($\underline{C}CO_2H$), 44.9 (CH_2Cl), and 32.33, 31.71, 26.53 and 26.23 (4 x CH_2) ppm.

2-Ethenyldodecanoic acid 5d.- 2-Butenoic acid **2** (1.55 g; 18 mmol), and 1-bromodecane **1d** (3.99 g, 18 mmol) gave a yellow oil (3.46 g; 85%) which when distilled led to the title acid as a colourless oil (2.73 g, 67 %), bp $_{2\ mm}$ 168-170 ° C; Found (MS, FAB+): $(M+1)^+$ 227.201283. $C_{14}H_{27}O_2$ requires 227.201105; ν_{max} 3500-2500 (OH), 1705 (C=O), 1635 (C=C), and 990 and 920 ($CH=CH_2$) cm^{-1}; δ_H 5.80 (1 H, ddd, J 17, 9 and 8 Hz, $\underline{CH}=CH_2$), 5.17 (2H , 2×d, J 17 and 10 Hz $CH=\underline{CH_2}$), 3.01 (1 H, dt, J 11 and 7.7 Hz, $C\underline{H}CO_2H$), 1.77 (2 H, m, CH_2), 1.56 (2 H, m, CH_2) and 1.4-1.1 (14 H, m, 7×CH_2) ppm; δ^{13}C 177.65 (CO_2H), 132.43 ($\underline{C}H=CH_2$), 114.53 ($CH=\underline{C}H_2$), 47.03 ($\underline{C}CO_2H$), and 28.88, 28.80, 26.48, 26.32, 26.22, 26.20, 23.86 and 19.59 (9×CH_2) and 11.02 (CH_3) ppm.

2-Ethenyltetradecanoic acid 5e.- Similarly 2-butenoic acid **2** (1.55 g; 18 mmol), and 1-bromododecane **1e** (4.5 g, 18 mmol), led to a yellow oil (3.66 g; 80 %). Crystallization from aqueous methanol gave colourless prisms (2.93 g; 64 %) mp 33-35 ° C; Found (MS, FAB+): $(M+1)^+$ 255.231763. $C_{16}H_{31}O_2$ requires 255.232406; ν_{max} 3500-2500 (O-H), 1710 (C=O), 1640 (C=C), and 990 and 920 ($CH=CH_2$) cm^{-1}; δ_H 5.80 (1 H, ddd, J 17, 9 and 8.7 Hz, $\underline{CH}=CH_2$), 5.17 (2H , 2×d, J 17 and 11 Hz, $CH=\underline{CH_2}$), 3.00 (1 H, dt, J 8 and 7.5 Hz, $C\underline{H}CO_2H$), 1.77 (2 H, m, CH_2), 1.56 (2 H, m, CH_2) and 1.4-1.1 (18 H, m, 9×CH_2) ppm; δ^{13}C 180.53 (CO_2H), 135.56 ($\underline{C}H=CH_2$), 117.63 ($CH=\underline{C}H_2$), 50.11 ($\underline{C}CO_2H$), and 32.00, 31.94, 29.65, 29.44, 29.37, 29.32, 26.98 and 22.72 (11×CH_2) and 14.15 (CH_3) ppm.

2-Benzyl-3-butenoic acid 5f.- According to the general method, 2-butenoic acid **2** (0.77 g; 9 mmol), and benzyl bromide **1f** (1.54 g, 9 mmol), after usual work-up, gave a yellow oil (1.32 g; 83.5%) which was distilled to give the title acid as a colourless oil (0.73 g, 54 %), bp $_{2\ mm}$ 100° C. δ_H 7.32-7.15 (H, m, Ar-H), 5.92-5.79 (1 H, ddd, J 17.4, 7.2, 6.3 Hz, $C\underline{H}=CH_2$), 5.16 (1 H, d, J 7.2 Hz, $CH=C\underline{H_2}$), 5.12 (1 H, d, J 17.4 Hz, $CH=C\underline{H_2}$), 3.34 (1 H, q, J 7.2 Hz, $C\underline{H}CO_2H$), 3.12 (1 H dd, J 13.5 and 7.5 Hz, $ArCH_2$) and 2.86 (1 H dd, J 13.8 and 7.5 Hz, $ArCH_2$) ppm.[3]

5-Chloro-2-ethenyl-2-methylpentanoic acid 6a.- According to the general method, 2-methyl-2-butenoic acid **3** (0.90 g; 9 mmol), and 1-chloro-3-bromopropane **1a** (0.9 ml; 9 mmol), after usual work-up, gave a yellow oil (1.42 g; 88.5 %); Found: (MS, CI+): $(M+1)^+$ 177.068369. $C_8H_{14}ClO_2$ requires 177.068233; ν_{max} 3500-2500 (OH), 1705 (C=O), 1645 (C=C), and 1020 and 930 ($CH=CH_2$) cm^{-1}; δ_H 5.9 (1 H, dd, J 17.1 and 11.1 Hz, $\underline{CH}=CH_2$), 5.2 (1 H, d, J 10.8 Hz, $CH=\underline{CH_2}$), 5.15 (1 H, d, J 18 Hz, $CH=\underline{CH_2}$), 3.5 (2 H, t, J, 6.0 Hz, CH_2Cl), 1.79-1.70 (4 H, m, 2×CH_2) and 1.27 (3 H, s, $\underline{CH_3}CCO_2H$) ppm; δ^{13}C 182.31 (CO_2H), 140.33 ($\underline{C}H=CH_2$), 114.79 ($CH=\underline{C}H_2$), 48.02 ($\underline{C}CO_2H$), 45.08 (CH_2Cl), 36.00 and 28.07 (2×CH_2), and 20.44 (C2-CH_3) ppm.

6-Chloro-2-ethenyl-2-methylhexanoic acid 6b.- By the same procedure, 2-methyl-2-butenoic acid **3** (0.9 g; 9 mmol), and 1-chloro-4-bromobutane **1b** (1 ml; 9 mmol), gave the title compound as a yellow oil

(1.48 g; 87%). Found: (MS, CI+): $(M+1)^+$ 191.084308. $C_9H_{16}ClO_2$ requires 191.083883; ν_{max} 3500-2500 (OH), 1700 (C=O), 1645 (C=C), and 1020 and 930 ($CH{=}CH_2$) cm^{-1}; δ_H 5.9 (1 H, dd, J 17.4 and 10.5 Hz, $\underline{CH}{=}CH_2$), 5.15 (1 H, d, J 10.2 Hz, $CH{=}\underline{CH_2}$), 5.1 (1 H, d, J 18 Hz, $CH{=}\underline{CH_2}$), 3.5 (2 H, t, J 6.6 Hz, CH_2Cl), 1.79-1.35 (6 H, m, $3{\times}CH_2$) and 1.27 (3 H, s, $\underline{CH_3}CCO_2H$) ppm; $\delta^{13}C$ 182.77 (CO_2H), 140.69 ($\underline{C}H{=}CH_2$), 114.47 ($CH{=}\underline{C}H_2$), 48.38 ($\underline{C}CO_2H$), 44.68 (CH_2Cl) , 38.04, 32.85 and 21.94 ($3{\times}CH_2$), and 20.16 (CH_3) ppm.

7-Chloro-2-ethenyl-2-methylheptanoic acid 6c.- This was obtained from 2-methyl-2-butenoic acid **3** (0.90 g; 9 mmol), and 1-chloro-5-bromopentane **1c** (1.2 ml; 9 mmol), as a yellow oil (1.53 g; 83%). Found: (MS, CI+): $(M+1)^+$ 205.099260. $C_{10}H_{18}ClO_2$ requires 205.099533; ν_{max} 3500-2500 (OH), 1705 (C=O), 1645 (C=C), and 1020 and 930 ($CH{=}CH_2$) cm^{-1}; δ_H 6.0 (1 H, dd, J 17.4 and 10.5 Hz, $\underline{CH}{=}CH_2$), 5.14 (1 H, d, J 10.2 Hz, $CH{=}\underline{CH_2}$), 5.1 (1 H, d, J 17.7 Hz, $CH{=}\underline{CH_2}$), 3.5 (2 H, t, J 6.6 Hz, CH_2Cl), 1.78-1.35 (8 H, m, $4{\times}CH_2$) and 1.26 (3 H, s, $\underline{CH_3}CCO_2H$) ppm; $\delta^{13}C$ 182.77 (CO_2H), 140.91 ($\underline{C}H{=}CH_2$), 114.25 ($CH{=}\underline{C}H_2$), 48.44 ($\underline{C}CO_2H$), 44.99 (CH_2Cl), 38.76, 32.48, 28.24 and 23.84 ($4{\times}CH_2$), and 20.20 (CH_3) ppm.

5-Chloro-2-(1-methylethenyl)pentanoic acid 7a.- According to the general method, 3-methyl-2-butenoic acid **4** (0.9 g; 9 mmol), and 1-chloro-3-bromopropane **1a** (0.9 ml; 9 mmol), gave acid **7a** as a yellow oil (1.46 g; 92%). Found: (MS, CI+): $(M+1)^+$ 177.068519. $C_8H_{14}ClO_2$ requires 177.068233; ν_{max} 3500-2500 (OH), 1700 (C=O), 1650 (C=C), and 895 ($R_2C{=}CH_2$) cm^{-1}; δ_H 4.95 (2 H, m, $R_2C{=}\underline{CH_2}$), 3.53 (2 H, m, CH_2Cl), 3.06 (1H, t, J 7.2 Hz, $\underline{CH}CO_2H$), 1.9-1.78 (4 H, m, $2{\times}CH_2$) and 1.75 (3 H, s, CH_3) ppm; $\delta^{13}C$ 179.83 (CO_2H), 141.29 ($\underline{C}H{=}CH_2$), 115.04 ($CH{=}\underline{C}H_2$), 52.21 ($\underline{C}HCO_2H$); 44.52 (CH_2Cl), 30.21 and 26.95 ($2{\times}CH_2$), and 19.66 (CH_3) ppm.

6-Chloro-2-(1-methylethenyl)hexanoic acid 7b.- Similarly 3-methyl-2-butenoic acid **4** (0.9 g; 9 mmol), and 1-chloro-4-bromobutaneane **1b** (1 ml; 9 mmol), led to the carboxylic acid **7b** as a yellow oil (1.57 g; 92%). Found (MS, FAB+): $(M+1)^+$ 191.083625 $C_9H_{16}ClO_2$ requires 191.083883; ν_{max} 3300-2600 (O-H), 1700 (C=O), 1645 (C=C), and 890 ($CR_2{=}CH_2$) cm^{-1}; δ_H 4.92 (2 H, m, $CR_2{=}CH_2$), 3.5 (2 H, t, J 6.6 Hz, CH_2Cl), 3.02 (1H, t, J 7.5 Hz, $\underline{CH}CO_2H$),1.76 (3H, s, CH_3) and 1.73-1.25 (6 H, m, $3{\times}CH_2$) ppm; $\delta^{13}C$ 179.9 (CO_2H), 141.6 ($\underline{C}{=}CH_2$), 114.7 ($C{=}\underline{C}H_2$), 52.78 ($\underline{C}CO_2H$), 44.67 (CH_2Cl) , 32.3, 28.99 and 24.67 ($3{\times}CH_2$), and 20.02 (CH_3) ppm.

7-Chloro-2-(1-methylethenyl)heptanoic acid 7c.- According to the general method, 3-methyl-2-butenoic acid **4** (0.90 g; 9 mmol), and 1-chloro-5-bromopentane **1c** (1.2 ml; 9 mmol), after usual work-up, gave the spectroscopically pure title acid as a yellow oil (1.78 g; 96%). Found (MS, FAB+): $(M+1)^+$ 205.099720. $C_{10}H_{18}Cl\,O_2$ requires 205.099533; ν_{max} 3400-2500 (O-H), 1700 (C=O), 1645 (C=C), and 895 ($R_2C{=}CH_2$) cm^{-1}; δ_H 4.92 (2 H, m, $R_2C{=}\underline{CH_2}$), 3.5 (2 H, t, J 6.6 Hz, CH_2Cl), 3.0 (1H, t, J 7.5 Hz, $\underline{CH}CO_2H$), 1.75 (3H, s, CH_3) and 1.61-1.26 (8 H, m, $4{\times}CH_2$) ppm; $\delta^{13}C$ 179.44 (CO_2H), 141.82 ($\underline{C}{=}CH_2$), 114.52 ($C{=}\underline{C}H_2$), 52.73 ($\underline{C}CO_2H$), 44.95 (CH_2Cl) , 32.33, 29.58, 26.62 and 26.62 ($4{\times}CH_2$), and 20.06 (CH_3) ppm.

General procedure for ozonation of 2-ethenyl alkanoic acids .- Ozone was bubbled through a stirred solution of the ethenyl alkanoic acid (7 mmol) in dichloromethane (30 ml) at -70°C, in a cylindrical reactor, provided with a porous glass tipped inlet tube, till the solution became persistently blue. Argon or nitrogen was then bubbled through the solution for 10 min. For ozonations to be followed by treatment with dimethyl sulfide, 70 ml of dichloromethane with 0.7 ml of pyridine was used as solvent. The cleavage reagent {triethylamine; 21 mmol), dimethyl sulfide (31 mmol) or triphenylphosphine (14 mmol)} was added, and the stirred solution allowed to warm up and stirred for the times given in Tables 2 and 3 after monitoring by TLC.

Work-up procedures were carried out as required according to the reagents.

a) For triethylamine: The reaction mixture was poured into water (40 ml) and extracted with dichloromethane. The organic layer was washed with 5% hydrochloric acid and brine, and dried, and the solvent evaporated.

b) For dimethyl sulfide: The reaction mixture was poured into water (40 ml). The organic layer was washed with 10% sodium bicarbonate, 5% hydrochloric acid and brine, and dried, and the solvent evaporated.

c) For triphenylphosphine: The solvent was evaporated and ethyl ether was added. The precipitate of triphenylphosphine oxide was filtered and washed with 30 ml of ethyl ether. The solvent was evaporated, and the residue chomatographed through a column of silica gel and elution with hexane/ether.

General procedure for the ozonolysis of 2-ethenyl alkanoic acids 5 in methanol.- The 2-ethenyl alkanoic acids **5** (7.7 mmol) in 15 ml of dry methanol was ozonized as described above, potassium iodide (3.9 g) and glacial acetic acid (3.9 ml) were added to the stirred solution at -70° C. The reaction solution was stirred for 1 h at rt. 10% sodium thiosulfate solution was added till the dark colour of the solution fainted. The solution was saturated with brine and extracted with dichloromethane. The organic layer was washed with water and dried, and the solvent evaporated.

General method for acetalization of aldehydes.- A solution of the aldehyde (5.5 mmol), ethylene glycol (8.2 mmol), p-toluenesulfonic acid (0.32 g) and benzene (50 ml) was heated under reflux in a Dean-Stark water separator. The reaction was monitored by TLC till no further change was observed. The mixture was then washed with 10% sodium bicarbonate and brine. The organic layer was dried over magnesium sulfate and the solvent evaporated. The crude acetals were purified by bulb to bulb distillation.

5-Chloropentanal 8a.- Ozonation of 5-chloro-2-ethenylpentanoic acid **5a** (1.29 g, 7.9 mmol) in methanol with KI as cleaving reagent, led to the spectroscopically pure title aldehyde as a colourless oil (0.87 g, 91%); ν_{max} 2950 and 2725 (CHO), 1723 (C=O), and 654 (CCl) cm^{-1} ; δ_H 9.75 (1H, t, J 1.2 Hz, CHO), 3.53 (2 H, t, J 6.1 Hz, CH_2Cl), 2.4 (2H, m, $\underline{CH_2}$-CHO), and 1.80-1.73 (4 H, m, 2×CH_2) ppm; $\delta^{13}C$ 201.82 (CHO), 44.43 (CH_2Cl), 42.91 ($\underline{CH_2}$-CHO), and 31.7 and 19.3 (2×CH_2) ppm. [7, 8, 9, 15, 16]

2-(4-Chlorobutyl)-1,3-dioxolane 13a.- 5-Chloropentanal **8a** (0.71 g, 5.9 mmol) gave the crude title dioxolane as a dark oil (0.95 g, 98%) which was distilled to give a colourless oil (0.79 g, 80 %), bp_{3mm} 72° C.

Found: (MS, CI+): $(M)^+$ 164.055493. $C_7H_{13}ClO_2$ requires 164.060408; ν_{max} 1136 (C-O), and 949 (CCl) cm^{-1}; δ_H 4.83 (1H, t, J 4.5 Hz, O-CH-O), 3.95-3.81 (4 H, m, OCH_2CH_2O), 3.51 (2H, t, J 6.6 Hz, CH_2Cl), and 1.80-1.57 (6 H, m, 3×CH_2) ppm; $\delta^{13}C$ 104.18 (O-CH-O), 64.80 (OCH_2CH_2O), 44.76 (CH_2Cl) , and 32.9, 32.34 and 21.29 (3×CH_2) ppm.

6-Chlorohexanal 8b.- Ozonation of 6-chloro-2-ethenyhexanoic acid **5b** (1.37 g, 7.7 mmol), in methanol, and reduction with KI, led to a colourless oil (0.87 g, 84 %); ν_{max} 2940, 2720 (CHO), 1720 (C=O), and 730 (CCl) cm^{-1} ; δ_H 9.75 (1H, t, J 1.2 Hz, CHO), 3.54 (2 H, t, J 6.6 Hz, CH_2Cl), 2.43 (2H, dt, J 6.9 and J 1.2 Hz, $\underline{CH_2}$-CHO), and 1.80-1.40 (6 H, m, 3×CH_2) ppm; $\delta^{13}{}_C$ 202.16 (CHO), 44.65 (CH_2Cl) , 43.62 ($\underline{CH_2}$-CHO), and 32.24, 26.33 and 21.39 (3×CH_2) ppm. [10, 15, 16]

2-(5-Chloropentyl)-1,3-dioxolane 13b.- This was obtained from 6-chlorohexanal **8b** (0.79 g, 5.8 mmol) as a dark oil (0.97 g, 94%) which was distilled to give a colourless oil (0.80 g, 77.5 %), $bp_{1.5\ mm}$ 72° C. Found; C, 53.66; H, 8.40; Cl, 20.22. $C_8H_{15}ClO_2$ requires C, 53.78; H, 8.46; Cl, 19.84 %; ν_{max} 1136 (C-O), and 949 (CCl) cm^{-1} ; δ_H 4.81 (1H, t, J 4.5 Hz, O-CH-O), 3.94-3.8 (4 H, m, OCH_2CH_2O), 3.5 (2H, t, J 6.8 Hz, CH_2Cl), and 1.9-1.40 (8 H, m, 4×CH_2) ppm; $\delta^{13}C$ 101.19 (O-CH-O), 61.72 (OCH_2CH_2O), 41.81 (CH_2Cl) , and 30.53, 29.38, 23.65 and 20.16 (4×CH_2) ppm.

7-Chloroheptanal 8c.- Ozonation of 7-chloro-2-ethenylheptanoic acid **5c** (1.47 g, 7.7 mmol) in methanol and reduction with KI, led to a colourless oil (0.96 g, 83 %); ν_{max} 2935, 2860 (CHO), 1724 (C=O), and 728 (CCl) cm^{-1} δ_H 9.74 (1H, t, J 1.2 Hz, CHO), 3.5 (2 H, t, J 6.7 Hz, CH_2Cl), 2.42 (2H, dt, J 6.5 and J 1.5 Hz, $\underline{CH_2}$-CHO), and 1.95-1.25 (8 H, m, 4×CH_2) ppm. [16]

2-(6-Chlorohexyl)-1,3-dioxolane 13c.- 7-Chloroheptanal **8c** (0.81 g, 5.5 mmol) gave dioxolane **13c** as a dark oil (0.89 g, 84 %), which was distilled to give a colourless oil (0.74.5 g, 79 %) ,$bp_{2\ mm}$ 74° C. Found; C, 56.04; H, 8.84; Cl, 18.75. $C_9H_{17}ClO_2$ requires C, 56.10; H, 8.89; Cl, 18.40 %; ν_{max} 1136 (C-O), and 949 (CCl) cm^{-1} ; δ_H 4.82 (1H, t, J 4.8 Hz, O-CH-O), 3.95-3.81 (4 H, m, OCH_2CH_2O), 3.5 (2H, t, J 6.45 Hz, CH_2Cl), and 1.75-1.37 (10 H, m, 5×CH_2) ppm; $\delta^{13}C$ 101.34 (O-CH-O), 61.70 (OCH_2CH_2O), 41.91 (CH_2Cl), and 30.62, 29.35, 25.63, 23.63 and 20.71 (5×CH_2) ppm.

Dodecanal 8d.- Ozonation of 2-ethenyldodecanoic acid **5d** (1.29 g, 5.7 mmol) in methanol and reduction with KI, led to a spectroscopically pure colourless oil (0.87 g, 83%); ν_{max} 2950, 2725 (CHO), 1723 (C=O), and 654 (CCl) cm^{-1}; δ_H 9.75 (1H, t, J 1.2 Hz, CHO), 2.4 (2H, t, J 6.5 Hz, $\underline{CH_2}$-CHO), 1.77 (2H, q, J 6.7 Hz, C3-H), 1.4-1.1 (16 H, m, 8×CH_2) and 0.86 (3H, t, J 6.5 Hz, CH_3) ppm. [35]

Tetradecanal 8e.- Ozonation of 2-ethenyltetradecanoic acid **5e** (1.03 g, 4.0 mmol) in methanol, and reduction with KI led to a spectroscopically pure colourless oil (0.80 g, 92%); ν_{max} 2950, 2720 (CHO), 1720 (C=O), and 654 (CCl) cm^{-1}; δ_H 9.74 (1H, t, J 1.7 Hz, CHO), 2.4 (2H, dt, J 7.4 and 1.9, $\underline{CH_2}$-CHO), 1.6 (2H, q, J 7.2, C3-H), and 1.4-1.1 (20 H, m, 10×CH_2) and 0.86 (3H, t, J 6.5 Hz, CH_3) ppm. [35]

2-(Tridecanyl)-1,3-dioxolane 13e.- Tetradecanal **8e** (0.73 g, 3.44 mmol) gave the crude title dioxolane as a dark oil (0.85 g, 96%), which was distilled to give a white waxy material (0.58 g, 66 %); ν_{max} and 1136 (C-O), cm^{-1} ; δ_H 4.82 (1H, t, J 4.8 Hz, O-CH-O), 3.95-3.81 (4 H, m, OCH_2CH_2O), 1.61 (2 H, q, J 6.2 Hz, $\underline{CH_2}$-C2), 1.4-1.1 (22 H, m, 11×CH_2) and 0.86 (3H, t, J 6.1 Hz, CH_3) ppm; δ^{13}c 104.72 (O-CH-O), 64.84 (OCH_2CH_2O), 34.27, 31.94, 29.71, 29.68, 29.67, 29.58, 29.55, 29.46, 29.41, 28.85, 24.12 and 22.71 (12×CH_2) and 14.15 (CH_3) ppm.[34]

3-Phenylpropanal 8f.- Ozonation of 2-benzylbut-3-enoic acid **5f** (0.53 g; 3 mmol) in methanol as above led to phenylpropanal **8f** as a pale yellow oil (0.36 g; 89.5 %), which was distilled, to give a spectroscopically pure colourless oil (0.31 g; 77 %) $bp_{3\ mm}$78° C. δ_H 9.82 (1 H, t, J 1.5 Hz, CHO), 7.3-7.2 (5 H, m, Ar-H), 2.95 (2 H, t, J 7.5 Hz, CH_2) and 2.76 (2 H, t, J 7.5 Hz, CH_2) ppm.[35]

5-Chloro-2-methylpentanal 9a.- Ozonation of 5-chloro-2-ethenyl-2-methylpentanoic acid **6a** (1.3 g, 7.35 mmol) in dichloromethane and cleavage with triethylamine, led to a colourless oil (0.70 g, 71%). Found (MS, CI+): $(M+1)^+$ 135.057838. $C_6H_{12}ClO$ requires 135.057668; ν_{max} 2810, 2720 (CHO), 1720 (C=O), 1380 (CH_3), and 720 (C-Cl) cm^{-1}; δ_H 9.6(1H, d, J 1.2 Hz, CHO), 3.5 (2 H, t, J 6.6 Hz, CH_2Cl), 2.38 (1H, m, $\underline{CH}CO$), 1.82-1.73 (4 H, m, 2×CH_2) and 1.1 (3H, d, J 7.5 Hz, CH_3) ppm.[8]

6-Chloro-2-methylhexanal 9b.- Ozonation of 6-chloro-2-ethenyl-2-methylhexanoic acid **6b** (1.31 g, 6.9 mmol) in dichloromethane and cleavage with triethylamine, led to a colourless oil (0.75 g, 73 %. Found (MS, CI+): $(M+1)^+$ 149.073273. $C_7H_{14}ClO$ requires 149.073318; ν_{max} 2810,2720 (CHO), 1710 (C=O), 1380 (CH_3), and 725 (C-Cl) cm^{-1} ; δ_H 9.6(1H, d, J 1.65 Hz, CHO), 3.5 (2 H, t, J 6.6 Hz, CH_2Cl), 2.33 (1H, m, $\underline{CH}CO$), 1.81-1.54 (6 H, m, 3×CH_2) and 1.1 (3H, d, J 7 Hz, CH_3) ppm; δ^{13}c 204.76 (CHO), 46.08 ($\underline{CH}CO$), 44.61 (CH_2Cl), 32.3, 29.56 and 24.18 (3×CH_2), and 13.26 (CH_3) ppm.

7-Chloro-2-methyl-heptanal 9c.- Ozonation of 7-chloro-2-ethenyl-2-methylheptanoic acid **6c** (1.50 g, 7.3 mmol) in dichloromethane and cleavage with triethylamine, led to a colourless oil (0.91 g, 77%). Found (MS, EI+): $(M-1)^+$ 161.073174. $C_8H_{14}ClO$ requires 161.073318 ; ν_{max} 2810,2720 (CHO), 1720 (C=O), 1380 (CH_3), and 720 (CCl) cm^{-1} ; δ_H 9.6(1H, d, J 2.1 Hz, CHO), 3.5 (2 H, t, J 6.3 Hz, CH_2Cl), 2.33 (1H, m, $C\underline{H}CHO$), 1.77-1.30 (8 H, m, 4×CH_2) and 1.06 (3H, d, J 6.9 Hz, CH_3) ppm; δ^{13}c 201.94 (CHO), 43.07 ($\underline{C}H_2CO$), 41.80 (CH_2Cl) , 29.23, 27.16, 23.74 and 23.1 (4×CH_2), and 10.23 (CH_3) ppm.

Ozonation of 5-chloro-2-(1-methylethenyl)pentanoic acid 7a.-

a) Ozonation of 5-chloro-2-(1-methylethenyl)pentanoic acid **7a** (1.30 g, 7.4 mmol) in dichloromethane (76 ml) pyridine (0.76 ml), and reduction with dimethyl sulfide, led to a green oil (0.84 g, 84%), which was distilled to give a colourless oil of 6-chloro-2-hexanone **10a** (0.51g, 51%), bp $_{3.5\ mm}$ 52° C (lit.[18] bp $_{2\ mm}$ 40-55° C); ν_{max} 1720 (C=O), 1380 (CH_3), and 720 (CCl) cm^{-1}; δ_H 3.5 (2 H, t, J 6.4 Hz, CH_2Cl), 2.44 (2H, t, J 6.8 Hz, $\underline{CH_2}CO$), 2.11 (3H, s, CH_3) and 1.77-1.68 (4 H, m, 2×CH_2) ppm; δ^{13}c 208.27 (C=O), 44.59 (CH_2Cl), 42.61 ($\underline{C}H_2CO$), 31.81and 29.85 (2×CH_2), and 20.96 (CH_3) ppm.

b) Ozonation of the same acid **7a** (1.41 g; 8 mmol) in diclhoromethane (35 ml), cleavage of the ozonide with triethylamine (3.3 ml; 24 mmol), and work-up as described in general method led to an oil (0.81 g). Column chromatography separation of this allowed isolation of 6-chloro-3-methylene-2-hexanone **12a** as a colourless oil (0.44 g; 38 %). ν_{max} 1690 (C=O), 1630 (C=C) and 720 (C-Cl) cm $^{-1}$; δ_H 6.06 (1 H; s, $C{=}CH_2$), 5.84 (1 H; s, $C{=}CH_2$), 3.51 (2 H, t, J 6.6 Hz, CH_2Cl), 2.41 (2 H; t, J 6.3 Hz, (CH_2), 2.33 (3 H, s, CH_3) and 1.88 (2 H, dt, J 7.2 and 6.6 Hz) ppm; [36] δ^{13}C 196 (C=O), 144.42 ($C{=}\underline{C}H_2$), 123.00 ($\underline{C}{=}CH_2$), 41.27 (CH_2Cl), 28.09 (CH_2), 24.96 (CH_2) and 22.72 (CH_3) ppm. Further elution gave 6-chloro-2-hexanone **10a** (0.28 g; 26 %), as above.

7-chloro-2-heptanone 10b.- Ozonation of 6-chloro-2-(1-methylethenyl)hexanoic acid **7b** (1.47 g, 7.7 mmol) in dichloromethane (79 ml) and pyridine (0.8 ml), and reduction with Me_2S led to a green oil (1.20 g, 98%), which was distilled to give the chloro ketone **10b** as a colourless oil, bp $_{5\ mm}$ 70° C (0.67 g, 58%) (lit.[18] bp $_{17\ mm}$ 97-103° C); ν_{max} 1715 (C=O), 1380 (CH_3), and 720 (C-Cl) cm^{-1} ; δ_H 3.49 (2 H, t, J 6.9 Hz, CH_2Cl), 2.44 (2H, t, J 6.6 Hz, $\underline{CH_2}CO$), 2.1 (3H, s, CH_3), 1.73 (2H, q, J 6.6 Hz, CH_2), 1.54 (2H, q, J 7.2 Hz, CH_2) and 1.45-1.36 (2H, m, CH_2) ppm; δ^{13}C 208.7 (C=O), 44.7 (CH_2Cl), 43.38 ($\underline{CH_2}CO$), 33.32, 29.88 and 26,33 ($3\times CH_2$), and 22.91 (CH_3) ppm.

8-chloro-2-octanone 10c.- Ozonation of 7-chloro-2-(1-methylethenyl)octanoic acid **7c** (1.57 g, 7.7 mmol) in dichloromethane (79 ml) and pyridine (0.8 ml), and reduction with Me_2S, led to a green oil (1.21 g, 97%), which was distilled to give the chloro ketone **10c** as a colourless oil, bp $_{4.5\ mm}$ 77° C (0.79 g, 63%) (lit.[18] bp $_{0.01\ mm}$ 49-50° C); ν_{max} 1720 (C=O), 1380 (CH_3), and 720 (C-Cl) cm^{-1} ; δ_H 3.47 (2 H, t, J 6.6 Hz, CH_2Cl), 2.38 (2H, t, J 6.9 Hz, $\underline{CH_2}CO$), 2.07 (3H, s, CH_3), 1.71 (2H, q, J 6.9 Hz, CH_2), 1.53 (2H, q, J 7.5 Hz, CH_2) and 1.41-1.22 (4 H, m, $2\times CH_2$) ppm; δ^{13}C 209.02 (C=O), 44.99 (CH_2Cl), 43.52 ($\underline{CH_2}CO$), 32.35, 29.94, 28.36 and 26.62 ($4\times CH_2$), and 23.54 (CH_3) ppm.

Acknowledgements

The present work has been financed by Dirección General de Investigación Científica y Técnica (DGICYT).

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(*Received in UK* 25 *April* 1997; *revised* 6 *June* 1997; *accepted* 12 *June* 1997)