# Conjugate Additions to α,β-Unsaturated Sulphoxides: Syntheses of Cyclopentenones and 9-Deoxyprostanoids

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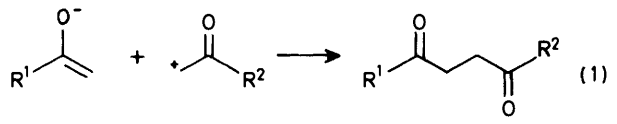
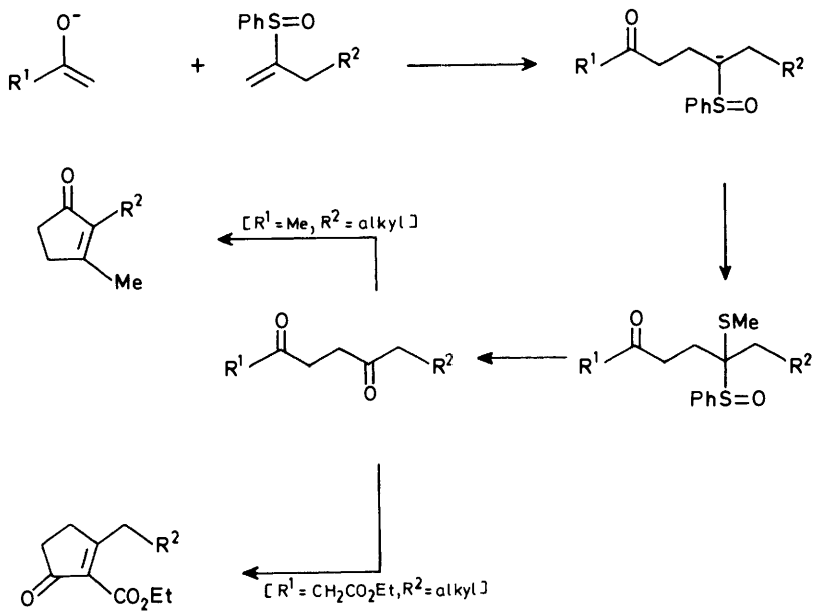
1,4-Dicarbonyl compounds, and hence cyclopentenone derivatives, were prepared by conjugate additions of enolate and related anions to α,β-unsaturated sulphoxides, followed by sulphoxide–ketone transformations. These transformations involved trapping the intermediate α-sulphinyl carbanions with dimethyl disulphide to give thioacetal monoxide derivatives, or Pummerer rearrangements of the sulphoxides to give alkenyl sulphides. 3-Substituted 2-ethoxycarbonylcyclopentenones prepared in this way were converted into 9-deoxyprostanoids and their 12-ethoxycarbonyl derivatives, the latter by use of 2-phenylsulphinyloct-1-en-3-one as an electrophilic prostanoid β-side-chain precursor.

The widespread occurrence of cyclopentenone rings in compounds of biological and commercial interest, such as the prostaglandins,[1] cyclopentanoid antibiotics,[2] rethrolones,[3] and jasmonoids,[4] has stimulated the development of many novel methods for their construction,[5] but for this purpose the well established intramolecular aldolization of 1,4-dicarbonyl compounds is still useful.[6] The appropriate 1,4-dicarbonyl compounds have been assembled in many ways,[6,7] but the conceptually simple combination of enolate anions and α-oxocarbocation equivalents [equation (1)] has been relatively little


(1)

exploited because there are few synthons for the cationic component: ketene thioacetal monoxides,[8] 2-(*N*-methylanilino)-acrylonitrile,[9] nitroethenes,[10] and α-bromoketones[6] have been used. We envisaged that α,β-unsaturated sulphoxides would be suitable synthons, bearing in mind that they are subject to conjugate addition,[11,12] and that it should be possible (see later) to convert suitable oxosulphoxides into 1,4-diketones. The ready availability of α,β-unsaturated sulphoxides bearing additional functional groups enhanced the potential scope of the procedure.[13] Our interest in it arose from a requirement for convenient syntheses of simple 9-deoxyprostanoids (**46**)—(**55**), and related 12-ethoxycarbonyl derivatives (**74**)—(**77**), which were chosen in order to examine relationships between biological activity and structure. It was known that 9-deoxyprostaglandin $E_1$,[14] (**46**, $R^1 = CO_2H$), a variety of 12-substituted prostanoids,[15] and other prostanoids in which the 1-carboxy group was replaced by a methyl[16] or hydroxymethyl group[17] exhibited biological activity which differed from that of the natural prostaglandins.

It was first necessary to establish if simple enolate anions would add conjugatively to α-alkyl-α,β-unsaturated sulphoxides under aprotic conditions, since our stratagem for the generation of 1,4-diketones involved the trapping of the intermediate sulphoxide-stabilized carbanions with a disulphide to form a thioacetal monoxide, which would subsequently be hydrolysed (Scheme). Previous examples of conjugate additions under aprotic conditions referred to vinyl sulphoxides lacking

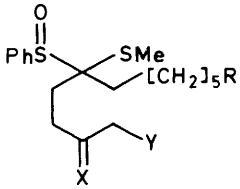



**Scheme.**

an α-alkyl substituent.[11] Most conjugate additions to α,β-unsaturated sulphoxides have been performed under protic conditions,[12] where the intermediate anions were immediately quenched, and the reactions consequently were driven in the desired direction. The nucleophiles of interest to us were acetone enolate anion, and the dianion of ethyl 3-oxobutanoate,[18] which were chosen because they would lead to 1,4-dicarbonyl compounds which would undergo intramolecular aldolization regiospecifically in two different directions (Scheme).[19,20]

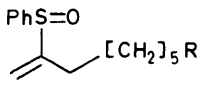
The lithium enolate from acetone, generated by use of lithium tetramethylpiperidide in tetrahydrofuran (THF), reacted with 2-phenylsulphinyloct-1-ene (**1**) at room temperature during 18 h to give 5-phenylsulphinylundecan-2-one (**3**) (63%).[21] In view of the greater acidity of acetone compared with dialkyl sulphoxides (by *ca.* 9 $pK_a$ units)[22] this result was unpredictable, though gratifying. Recently it was shown that the lithium enolate of acetone did not add to an α,β-unsaturated sulphone, although the corresponding potassium enolate did.[23] Faster addition to the alkenyl sulphoxide (**1**) occurred with the lithio derivative of acetone dimethylhydrazone,[24] which, in the presence of dimethyl sulphide–copper(I) bromide complex,[25] gave the adduct (**4**) after 30 min in THF at 0 °C. In the absence of copper catalysis, of which this is the first example of its kind, Michael-type addition proceeded in poor yield. The adduct (**4**) was hydrolysed by aqueous copper(II) acetate[26] to the oxosulphoxide (**3**) [57% from (**1**)]. The more reactive lithio sodio dianion from ethyl 3-oxobutanoate added to the alkenyl sulphoxide (**1**) within 5 min at O °C in THF to give the adduct (**5**) (80%), which on hydrolysis and decarboxylation gave the oxosulphoxide (**3**) (80%). Treatment of the oxosulphoxide (**3**) with trifluoroacetic acid and pyridine in dichloromethane gave, *via* a Pummerer rearrangement,[27] a mixture of isomeric oxo alkenyl sulphides (**7**) and (**10**), which presumably contains the isomer (*E*)-(**7**) previously synthesized by Cookson and Parsons by a different method.[28] These isomers could not be separated by chromatography, but treatment of the mixture with trifluoroacetic acid for 5 min at room temperature gave undecane-2,5-dione (**13**) [65% from (**3**)], which cyclized to dihydrojasmone (**16**) in aqueous ethanolic sodium hydroxide.[19] Since 2-phenylsulphinyloct-1-ene (**1**) is readily prepared from oct-1-yne,[13] these represent convenient preparations of the perfume constituent (**16**).

Having established the feasibility of the conjugate additions, we turned to the sulphenylation of the intermediate anions, as outlined in the Scheme. The reaction mixture from acetone lithium enolate and 2-phenylsulphinyloct-1-ene (**1**), on being quenched (after 18 h) with dimethyl disulphide, gave only the oxosulphoxide (**3**): apparently, the long reaction time allowed the intermediate anions to be quenched by protons from an unidentified source. However, quenching the reaction mixture from the copper-catalysed addition of the lithio derivative of acetone dimethylhydrazone and the alkenyl sulphoxide (**1**) with dimethyl disulphide gave the doubly protected 1,4-diketone derivative (**18**), which on sequential hydrolysis with copper(II) acetate and trifluoroacetic acid gave first the oxothioacetal monoxide (**17**), and then undecane-2,5-dione (**13**) [54% from (**1**)]. The intermediates (**18**) and (**17**) decomposed on silica chromatography and were not fully characterized.

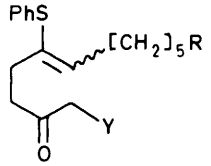


(17) X = O, Y = R = H
(18) X = $NNMe_2$, Y = R = H
(19) X = O, Y = $CO_2Et$, R = H
(20) X = O, Y = $CO_2Et$, R = $CH_2OH$

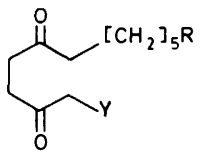
Treatment of the alkenyl sulphoxide (**1**) in sequence with the dianion of ethyl 3-oxobutanoate and dimethyl disulphide furnished the thioacetal monoxide derivative (**19**), which on brief exposure to trifluoroacetic acid in wet benzene was converted into the dioxoester (**14**). Cyclization of compound (**14**) to give ethyl 2-hexyl-5-oxocyclopent-1-enoate (**21**) occurred quantitatively under mild basic conditions. In this way the alkenyl sulphoxide (**1**) was converted into the cyclopentenone derivative (**21**) rapidly in 62% yield, without isolation of intermediates. The thioacetal monoxide derivative (**19**) decomposed on contact with silica, but it was isolated by rapid chromatography, and its structure was confirmed by n.m.r. spectroscopy (see Experimental section). The intermediate dianion (**23**) had undergone sulphenylation only adjacent to sulphur, as expected on the basis of the known reluctance of 'active' methylene compounds to react with disulphides.[29] Conditions for complete sulphenylation adjacent to the sulphoxide were not found; some (*ca.* 15%) of the oxosulphoxide ester (**5**) was always obtained after application of the addition–trapping–hydrolysis–cyclization sequence. Overall yields were not improved by use of diphenyl disulphide instead of dimethyl disulphide. However, the adduct (**5**) was also converted into the dioxoester (**14**) by treatment first with trifluoroacetic anhydride and pyridine to give a mixture of alkenyl sulphides (**8**) and (**11**) (83%), and then with mercury(II) chloride and cadmium carbonate in aqueous acetonitrile[30] to hydrolyse the vinyl sulphides (65%). Starting from 9-hydroxy-2-phenylsulphinylnon-1-ene (**2**), which was prepared by



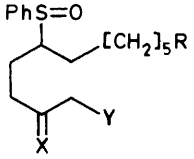
(1) R = H
(2) R = $CH_2OH$



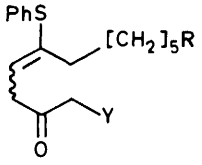
(7) Y = R = H
(8) Y = $CO_2Et$, R = H
(9) Y = $CO_2Et$, R = $OCOCF_3$



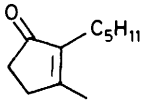
(13) Y = R = H
(14) Y = $CO_2Et$, R = H
(15) Y = $CO_2Et$, R = $CH_2OH$



(3) X = O, Y = R = H
(4) X = $NNMe_2$, Y = R = H
(5) X = O, Y = $CO_2Et$, R = H
(6) X = O, Y = $CO_2Et$, R = $CH_2OH$

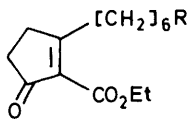


(10) Y = R = H
(11) Y = $CO_2Et$, R = H
(12) Y = $CO_2Et$, R = $OCOCF_3$

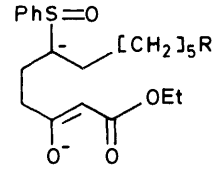


(16)

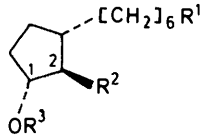
regioselective addition of benzenesulphenic acid to non-8-yn-1-ol,[13] the cyclopentenone derivative (**22**) was synthesized in 33% overall yield *via* the intermediates (**24**) (**20**), and (**15**), by use of the methods described earlier.



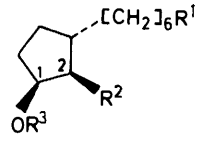
(21) R = H
(22) R = $CH_2OH$



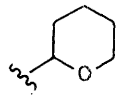
(23) R = H
(24) R = $CH_2O^-$



| | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|
| (25) | H | $CO_2Et$ | H |
| (26) | H | $CH_2OH$ | H |
| (27) | H | $CO_2Et$ | THP |
| (28) | H | $CH_2OH$ | THP |
| (29) | H | CHO | THP |
| (30) | $CH_2OTHP$ | $CO_2Et$ | H |
| (31) | $CH_2OTHP$ | $CO_2Et$ | THP |
| (32) | $CH_2OTHP$ | $CH_2OH$ | THP |
| (33) | $CH_2OTHP$ | CHO | THP |

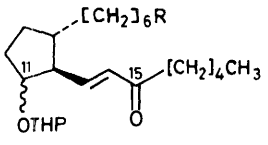


| | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|
| (34) | H | $CO_2Et$ | H |
| (35) | H | $CH_2OH$ | H |
| (36) | H | $CO_2Et$ | THP |
| (37) | H | $CH_2OH$ | THP |
| (38) | H | CHO | THP |
| (39) | $CH_2OTHP$ | $CO_2Et$ | H |
| (40) | $CH_2OTHP$ | $CO_2Et$ | THP |
| (41) | $CH_2OTHP$ | $CH_2OH$ | THP |
| (42) | $CH_2OTHP$ | CHO | THP |

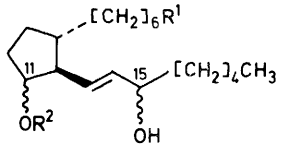
THP = 

Numbering scheme is that used for stereochemical assignments (see text). Systematic numbering is used in the Experimental section

With a convenient means of constructing 3-alkyl-2-ethoxycarbonylcyclopentenones in hand, the synthesis of the 9-deoxyprostanoids (**46**)—(**49**), (**54**), and (**55**) was straightforward (*cf.* ref. 14). Reduction of the cyclopentenone (**21**) by sodium borohydride[31] gave a mixture of *cis*- and *trans*-hydroxyesters (**25**) and (**34**), which were separated by chromatography.* Relative configurations were established by reduction of the isomeric hydroxyesters by lithium aluminium hydride to the diols (**26**) and (**35**), of which only one isomer, (**35**), gave a cyclic acetal on treatment with *p*-nitrobenzaldehyde, in accord with a *cis* relationship between the 1-hydroxy and 2-hydroxymethyl groups. Protection of the 1α-hydroxy group in the hydroxyester (**25**) as the tetrahydropyranyl ether (**27**) was followed in sequence by reduction of the ester group by lithium aluminium hydride to give the alcohol (**28**), and oxidation with Collins' reagent to give the aldehyde (**29**). With 1-tri-n-butylphosphoranylideneheptan-2-one this aldehyde, (**29**), afforded the enone (**43**), which on reduction and subsequent cleavage of the tetrahydropyranyl ether gave a mixture of 11α,15α-dihydroxy-1-norprost-13-ene (**46**) and its 15β-isomer (**47**). These were separated by chromatography, and the less mobile isomer (**46**) was assigned the 15α-configuration by analogy with the reported chromatographic characteristics of 9-deoxyprostaglandin $E_1$ and its 15-epimer.[14] The *cis*-hydroxyester (**34**) was similarly converted into 11β,15α-dihydroxy-1-norprost-13-ene (**48**) and its 15β-isomer (**49**) *via* compounds (**36**)—(**38**): 1,11α,15α- and 1,11α,15β-trihy-



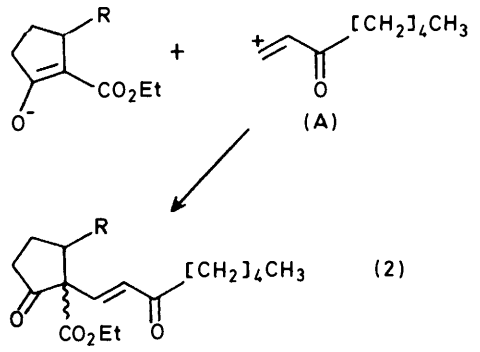
| | R | orientation at C-11 |
|---|---|---|
| (43) | H | α |
| (44) | $CH_2OTHP$ | α |
| (45) | $CH_2OTHP$ | β |



| | $R^1$ | $R^2$ | orientation at C-11 | orientation at C-15 |
|---|---|---|---|---|
| (46) | H | H | α | α |
| (47) | H | H | α | β |
| (48) | H | H | β | α |
| (49) | H | H | β | β |
| (50) | $CH_2OTHP$ | THP | α | α |
| (51) | $CH_2OTHP$ | THP | α | β |
| (52) | $CH_2OTHP$ | THP | β | α |
| (53) | $CH_2OTHP$ | THP | β | β |
| (54) | $CH_2OH$ | H | α | α |
| (55) | $CH_2OH$ | H | α | β |

* These compounds, and those derived from them, were racemic modifications. Only one enantiomer is depicted in each case, and the α,β convention is used here to describe stereochemistry in relation to an arbitrarily assigned α-configuration of the alkyl side-chains in the parent compounds (**25**) and (**34**).

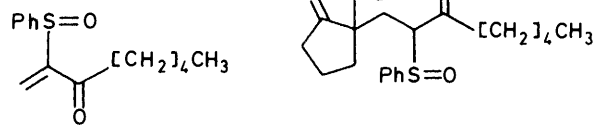
droxyprost-13-ene, (**54**) and (**55**), were obtained by similar procedures from the cyclopentenone (**22**). The 11β-isomers of the triols (**54**) and (**55**) were not prepared, but details for their acetal derivatives (**52**) and (**53**) are included in the Experimental section.




In order to synthesize 12-ethoxycarbonyl prostanoids we required a synthetic equivalent of the carbocation (**A**), to be employed as a precursor for the prostanoid β-side-chain [equation (2)]. Electrophilic β-side-chain precursors are scarce,[32] in contrast to the appreciable number of nucleophilic precursors,[33] and they tend to be unreactive, or non-stereospecific in the introduction of the double bond at C-13.[32] We considered that the oxo alkenyl sulphoxide (**56**) would be a good electrophilic synthon, since γ-oxo-α,β-unsaturated sulphoxides are good Michael acceptors, and β-oxosulphoxides thermolyse readily and specifically to (*E*)-enones.[34] The following exploratory experiments confirmed that view.

2-Phenylsulphinyloct-1-en-3-one (**56**) was prepared by oxidation of 3-hydroxy-2-phenylsulphinyloct-1-ene[13] with Jones reagent (80% yield). It reacted with methyl 2-oxocyclopentanecarboxylate in moist ether containing potassium carbonate to give the adduct (**57**) quantitatively. Under the same conditions with dimethyl malonate it gave the mono- and di-alkylated products (**58**) and (**61**), and with ethyl 3-oxobutanoate the products (**59**) and (**62**). Thermolysis of the adduct (**57**) in boiling toluene gave the (*E*)-enone (**60**) (81%) stereospecifically, and thermolysis of compound (**61**) for 5 min at 140 °C also proceeded stereospecifically to give the dimethyl malonate derivative (**63**) (86%). The adduct (**58**), on thermolysis at 140 °C for 15 min furnished the pyranone derivative (**64**) (55%) *via* the initially formed enone.

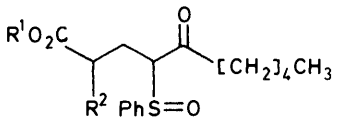
In the light of the preceding observations the construction of 12-ethoxycarbonyl prostanoids was straightforward. Reduction of the cyclopentenone derivatives (**21**) and (**22**) with sodium cyanoborohydride gave the oxoesters (**65**) and (**66**) respectively, in which the *trans* relationship between the ester group and neighbouring alkyl group was allocated on thermodynamic grounds. Treatment of the oxoester (**65**) with 2-phenylsulphinyloct-1-en-3-one (**56**) gave a mixture of diastereoisomeric adducts (**67**), which was immediately thermolysed in boiling toluene in the presence of trimethyl phosphite to give an inseparable mixture of α,β-unsaturated ketones (**69**) and (**70**). The oxoester (**66**) was similarly converted, *via* the adducts (**68**), into a mixture of enones (**71**) and (**72**). In each mixture the 12α-ethoxycarbonyl isomers, (**69**) and (**71**), predominated, the 12α:12β ratio being *ca.* 8:1, according to the relative intensities of the well separated $^1$H n.m.r. signals (see Experimental section) due to the vinyl protons for the constituent isomers. Allocations of configuration at C-12 followed from an interpretation of the $^{13}$C n.m.r. spectrum of the mixture of compounds (**71**) and (**72**), which included signals at $\delta_C$ 170.12 and 168.48 p.p.m. of relative intensity 1:10 due to the carbonyl carbon atom of the ester groups, and signals at $\delta_C$ 142.42 and 137.78 p.p.m. of relative intensity 11:2 due to the C-13 vinyl carbons. Bearing in mind that the 7-methylene group should



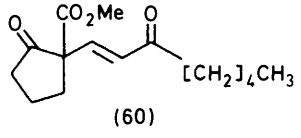

(**56**)



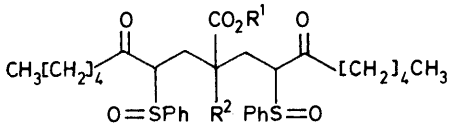

(**57**)



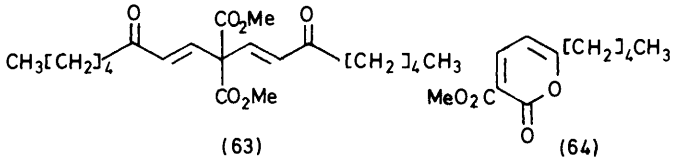

(**58**) $R^1$ = Me, $R^2$ = $CO_2$Me
(**59**) $R^1$ = Et, $R^2$ = COMe



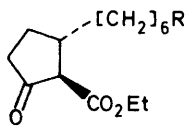

(**60**)



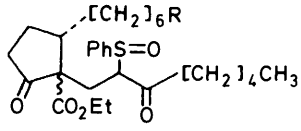

(**61**) $R^1$ = Me, $R^2$ = $CO_2$Me
(**62**) $R^1$ = Et, $R^2$ = COMe



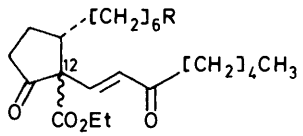

(**63**) (**64**)



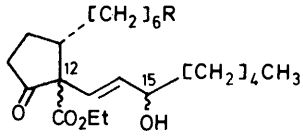
(65) R = H
(66) R = $CH_2OH$



(67) R = H
(68) R = $CH_2OH$

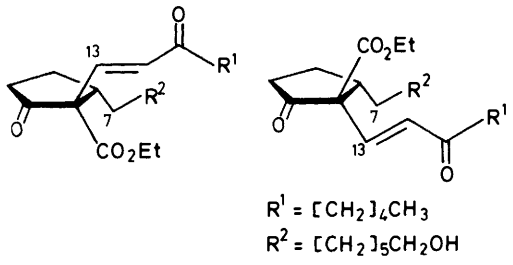


| | R | orientation of 12-$CO_2Et$ |
|---|---|---|
| (69) | H | α |
| (70) | H | β |
| (71) | $CH_2OH$ | α |
| (72) | $CH_2OH$ | β |
| (73) | $CO_2Me$ | α,β |



| | R | orientation of 12-$CO_2Et$ | 15-OH |
|---|---|---|---|
| (74) | H | α | α |
| (75) | H | α | β |
| (76) | $CH_2OH$ | α,β | α,β |
| (77) | $CO_2Me$ | α,β | α,β |

shield (by the γ-effect[35]) the *cis*-orientated ethoxycarbonyl carbon in (**71**), and the C-13 (vinyl) carbon in the *cis*-orientated side-chain in (**72**) (see Figure), the more intense signals at $\delta_C$ 168.48 and 142.42 p.p.m. were allocated to the ethoxycarbonyl carbon and C-13 vinyl carbon respectively in the 12α-ethoxycarbonyl isomer (**71**).



$R^1 = [CH_2]_4CH_3$
$R^2 = [CH_2]_5CH_2OH$

**Figure.**

Treatment of the mixture of enediones (**69**) and (**70**) with sodium cyanoborohydride[36] furnished a mixture of allylic alcohols, from which the major constituents (**74**) and (**75**) were separated by high-performance liquid chromatography (h.p.l.c.). These were oxidised separately with Jones reagent at −20 °C to afford the same enone (**69**)), which confirmed that the alcohols were 15-epimers. The products obtained by reduction of the mixture of hydroxy-enediones (**71**) and (**72**) with sodium cyanoborohydride could not be separated into their constituents by chromatography, nor could the hydroxy diesters (**77**), which were obtained by treatment of the mixture of (**71**) and (**72**) in succession with Jones reagent and diazomethane to give (**73**), followed by reduction with sodium cyanoborohydride. Attempts at separation were frustrated by the decomposition of the compounds, which consequently were characterized only by the spectroscopic properties of the mixtures.

## Experimental

M.p.s were determined with a Kofler block apparatus. Spectra were determined with a Perkin-Elmer 157G spectrophotometer, u.v. spectra with a Perkin-Elmer 559 spectrometer, and mass spectra with a Kratos MS25 or MS80 spectrometer. $^1H$ N.m.r. spectra were determined at 220 MHz (unless otherwise indicated), with a Perkin-Elmer R34 spectrometer, and refer to deuteriochloroform solutions with tetramethylsilane as internal standard: spectra at 400 MHz were determined with a Bruker WH400 instrument, and $^{13}C$ spectra with a JEOL PFT100 spectrometer. Column chromatography was performed with Merck 7736 60H silica gel, and preparative high-performance liquid chromatography with a 25 cm Spherisorb (15 μ) column coupled to a Cecil CE212 u.v. monitor and a Waters R401 differential refractometer. Ether refers to diethyl ether, and light petroleum to the fraction boiling between 40 and 60 °C (except where stated otherwise).

9-*Hydroxy*-2-*phenylsulphinylnon*-1-*ene* (**2**).—A mixture of non-8-yn-1-ol (10 g, 0.072 mol) and 1-cyano-2-phenylsulphinylethane[13] (2.6 g, 0.015 mol) was heated at 126 °C under nitrogen for 3 h. The solvent was removed under reduced pressure and the residue was chromatographed on silica and eluted with ether to give the *product* (**2**) (3.0 g, 78%) as an oil, $\nu_{max.}$(film) 3 400 (OH), 1 640 (C=C), and 1 050 $cm^{-1}$ (S=O); δ 7.55 (5 H, m, $C_6H_5$), 6.08 (1 H, s, C=C*H*H′), 5.60 (1 H, s, C=CH*H*′), 3.58 (2 H, t, *J* 7 Hz, $CH_2OH$), 2.05 (1 H, s, OH), and 2.00 (2 H, m, $C{=}CCH_2$); *m/z* ($M^+$) 266 (Found: C, 67.5; H, 8.3. $C_{15}H_{22}O_2S$ requires C, 67.6; H, 8.3%).

5-*Phenylsulphinylundecan*-2-*one* (**3**).—(*a*) A solution of 2,2,6,6-tetramethylpiperidine (979 mg, 6.95 mmol) in THF (15 ml) was treated with a solution of butyl-lithium (450 mg, 6.98 mmol) in hexane (4.65 ml) at 0 °C. After 10 min, acetone (492 mg, 8.47 mmol) was added, followed, after a further 10 min, by a solution of 2-phenylsulphinyloct-1-ene (**1**)[13] (1.0 g, 4.24 mmol) in THF (10 ml). The mixture was stirred for 24 h at room temperature, the reaction was quenched with saturated aqueous ammonium chloride (10 ml), and the mixture was worked up with ether in the usual way. Chromatography on silica (20 g) and elution with ether–light petroleum (4:1) furnished the *product* (**3**) (785 mg, 63%) as an oil, $\nu_{max.}$ ($CHCl_3$) 1 710 (C=O) and 1 015 $cm^{-1}$, δ 7.50 (5 H, m, $C_6H_5$), 2.64 (2 H, m, $CH_2CO$), 2.36 (1 H, m, CHSOPh), 2.12 (3 H, s, $COCH_3$), 1.40 (10 H, m, $[CH_2]_5$), and 0.82 (3 H, m, $CH_2CH_3$) (Found: $M^+$, 294.1647. $C_{17}H_{26}O_2S$ requires *M*, 294.1654).

(*b*) Butyl-lithium (0.62 g, 9.7 mmol) in hexane (7.7 ml) was added to a stirred solution of di-isopropylamine (0.92 g, 9.1 mmol) in THF (25 ml) at 0 °C under nitrogen. After 30 min a solution of acetone dimethylhydrazone (0.83 g, 8.3 mmol) in THF (5 ml) was added by syringe and the mixture was stirred for a further 30 min. This white suspension was added by syringe to a solution of dimethyl sulphide–copper(I) bromide complex (850 mg, 4.1 mmol) in a mixture of dimethyl sulphide (8 ml) and THF (8 ml) at 0 °C under nitrogen. A solution of 2-phenylsulphinyloct-1-ene (**1**) (1.0 g, 4.2 mmol) in dry THF (5 ml) was added and the mixture was stirred for 30 min at 0 °C. Dilution with ether and water, and the usual work-up with ether, gave an oil which was dissolved in THF (30 ml) and added to a solution of copper(II) acetate (1.2 g, 6 mmol) in water (30 ml). After 2 h the solvent was evaporated off, the residue was diluted with an aqueous solution (pH 8) of ammonium chloride and ammonium hydroxide and extracted with dichloromethane. The dried extract ($MgSO_4$) was evaporated, and the residue purified by chromatography as before to give the product (**3**) (709 mg, 57%).

(*c*) A solution of ethyl 3-oxo-6-phenylsulphinyldodecanoate (**5**) (see below) (2.3 g, 6.3 mmol) in 5% aqueous sodium hydroxide (40 ml) was stirred for 2 days at 20 °C. Acidification with 50% sulphuric acid followed by work-up with ether afforded an oil which was dissolved in acetone (60 ml). The solution was boiled for 6 h, the solvent removed by evaporation,

and the residue was purified as described above to give the product (**3**) (1.48 g, 80%).

*Ethyl* 3-*Oxo*-6-*phenylsulphinyldodecanoate* (**5**).—Ethyl 3-oxobutanoate (1.67 g, 0.0127 mol) was added to a stirred suspension of sodium hydride (50% dispersion in mineral oil; 0.67 g, 0.0139 mol) in dry THF (60 ml) at 0 °C under nitrogen. After 5 min, butyl-lithium in hexane (0.85 g, 1.33 mmol) was added, and the mixture was stirred for 15 min at 0 °C, and then cooled to − 20 °C. 2-Phenylsulphinyloct-1-ene (**1**) (3 g, 0.0127 mol) in dry THF (6 mml) was added, and the mixture was stirred for 1 h at −10 °C before being poured into a saturated solution of ammonium chloride (20 ml). Work-up with ether afforded an oil which was chromatographed on silica (65 g) and eluted with ether–light petroleum (3 : 1) to give the oily *product* (**5**) (4.65 g, 89%), $\nu_{max.}$(CHCl$_3$) 1 740 (CO$_2$Et), 1 715 (C=O), and 1 015 cm$^{-1}$ (S=O); δ 7.52 (5 H, m, C$_6$H$_5$), 4.20 (2 H, q, *J* 7 Hz, CO$_2$C*H*$_2$CH$_3$), 3.44 (2 H, s, COCH$_2$CO), 2.78 (1 H, m, C*H*SOPh), 2.59 (2 H, t, *J* 6 Hz, CH$_2$C*H*$_2$CO), 1.97 (2 H, m, C*H*$_2$CH$_2$CO), 1.32 (10 H, m, [CH$_2$]$_5$), 1.27 (3 H, t, *J* 7 Hz, CO$_2$CH$_2$C*H*$_3$), and 0.82 (3 H, m, CH$_2$C*H*$_3$) (Found: C, 65.45; H, 8.3; S, 8.8. C$_{20}$H$_{30}$O$_4$S requires C, 65.5; H, 8.25; S, 8.75%).

*Ethyl* 13-*Hydroxy*-3-*oxo*-6-*phenylsulphinyltridecanoate* (**6**).—Ethyl 3-oxobutanoate (5.86 g, 0.045 mol) and 9-hydroxy-2-phenylsulphinylnon-1-ene (**2**) (10 g, 0.038 mol) gave, by the procedure described above, the *product* (**6**) (10 g, 67%) as an oil, $\nu_{max.}$(film) 3 420 (OH), 1 740 (CO$_2$Et), 1 710 (C=O), and 1 030 cm$^{-1}$ (S=O); δ 7.51 (5 H, m, C$_6$H$_5$), 4.21 (2 H, q, *J* 7 Hz, CO$_2$C*H*$_2$CH$_3$), 3.6 (2 H, t, *J* 7 Hz, C*H*$_2$OH), 3.48 (2 H, s, COCH$_2$CO), 2.84 (1 H, m, C*H*SOPh), 2.6 (2 H, t, CH$_2$C*H*$_2$CO), 1.99 (2 H, m, C*H*$_2$CH$_2$CO), and 1.89 (2 H, m); *m/z* 396 (*M*$^+$) (Found: C, 63.4; H, 8.1. C$_{21}$H$_{32}$O$_5$S requires C, 63.6; H, 8.1%).

*Undecane*-2,5-*dione* (**13**).—(*a*) Trifluoroacetic anhydride (2.3 g, 0.011 mol) was added to a solution of 5-phenylsulphinylundecan-2-one (**3**) (330 mg, 1.1 mmol) and pyridine (0.3 ml) in dichloromethane (35 ml). After 1 h the solvent was evaporated off and the residue was treated with trifluoroacetic acid (5 ml) for 5 min at 20 °C. Neutralization with aqueous sodium hydrogen carbonate, and the usual work-up with ether, furnished a brown oil which was chromatographed on silica (13 g) and eluted with ether–light petroleum (13 : 7) to give the oily product (**13**) (134 mg, 65%), $\nu_{max.}$(CHCl$_3$) 1 710 cm$^{-1}$; δ 2.69 (4 H, m, 3- and 4-H$_2$), 2.45 (2 H, t, 6-H$_2$), 2.18 (2 H, s, 1-H$_3$), 1.54 (2 H, qn, *J* 7 Hz, 7-H$_2$), 1.26 (6 H, m, 8-, 9-, and 10-H$_2$), and 0.87 (3 H, t, *J* 7 Hz, 11-H$_3$).

(*b*) 2-Phenylsulphinyloct-1-ene (**1**) (1.0 g) was treated with the lithium derivative of acetone dimethylhydrazone and dimethyl sulphide–copper(I) bromide complex in the manner described above [see preparation of (**3**)]. After 30 min dimethyl disulphide (8 g, 0.084 mol) was added (instead of ether and water as previously), and the mixture was stirred for 30 min. Dilution with ether and water, and the usual work-up with ether, gave an oil which was dissolved in THF (30 ml) and added to a solution of copper(II) acetate (1.2 g, 6 mmol) in water (30 ml). After 2 h the solvent was evaporated off, the residue diluted with an aqueous solution of ammonium chloride and ammonium hydroxide, and the mixture extracted with dichloromethane. The extract was dried and evaporated, and the residue treated with trifluoroacetic acid (10 ml) for 30 min at 20 °C. Neutralization with aqueous sodium hydrogen carbonate, and work-up with ether, gave a brown oil which was chromatographed on silica as described above to give undecane-2,5-dione (460 mg, 59%).

The structure of the dione was substantiated as follows. The dione (**13**) (440 mg, 2.4 mmol) in a mixture of ethanol (22 ml) and 2% aqueous sodium hydroxide (22 ml) was boiled for 5 h under nitrogen. The usual work-up with ether, followed by chromatography [silica; ether–light petroleum (3 : 1)], gave dihydrojasmone (**16**) (261 mg, 65%) as an oil, $\nu_{max.}$(CHCl$_3$) 1 705 and 1 650 cm$^{-1}$; δ 2.47 (2 H, m, ring CH$_2$), 2.35 (2 H, m, ring CH$_2$), 2.25 (2 H, t, allylic CH$_2$), 2.04 (3 H, s, vinylic methyl), 1.55 (6 H, m, [CH$_2$]$_3$), and 0.86 (3 H, t, CH$_2$C*H*$_3$).

*Ethyl* 3,6-*Dioxododecanoate* (**14**).—(*a*) 2-Phenylsulphinyloct-1-ene (**1**) (24 g, 0.1 mol) in dry THF (50 ml) was added to a solution (prepared as described above) of the dianion of ethyl 3-oxobutanoate (15.9 g, 0.122 mol) in THF (350 ml) at −20 °C under nitrogen. After 15 min, a solution of dimethyl disulphide (29 g, 0.308 mol) in THF (30 ml) was added, and the mixture was shaken vigorously for 15 min. The solvent was evaporated off and the residue dissolved in a mixture of trifluoroacetic acid (30 ml) and wet benzene (200 ml). After 5 min, the mixture was concentrated under reduced pressure, the residual oil dissolved in ether (500 ml), and the ethereal solution shaken with 8% aqueous sodium hydroxide (100 ml) for 2 min [shaking for 10 min effected complete conversion of the dione (**14**) into the cyclopentenone (**21**)—see later]. The mixture was neutralized with dil. hydrochloric acid, and then worked up with ether in the usual way. Chromatography of the residue on silica (400 g) and elution with ether–light petroleum (2 : 3) gave ethyl 3,6-*dioxododecanoate* (**14**) (9.80 g, 37%) as an oil, $\nu_{max.}$(CHCl$_3$) 1 740 (CO$_2$Et) and 1 710 cm$^{-1}$ (C=O); δ 4.16 (2 H, q, *J* 7 Hz, CO$_2$C*H*$_2$CH$_3$), 3.46 (2 H, s, COCH$_2$CO), 2.72 (4 H, m, CO[CH$_2$]$_2$CO), 2.41 (2 H, t, *J* 7 Hz, COCH$_2$); *m/z* 256 (*M*$^+$) (Found: C, 65.8; H, 9.1. C$_{14}$H$_{24}$O$_4$ requires C, 65.6; H, 9.4%). Further elution gave, first, ethyl 2-hexyl-5-oxocyclopent-1-enecarboxylate (**21**) (6.34 g, 26%), and then ethyl 3-oxo-6-phenylsulphinyldodecanoate (**5**) (5.62 g, 15%).

(*b*) Trifluoroacetic anhydride (15.4 g, 0.073 mol) was added to a solution of ethyl 3-oxo-6-phenylsulphinyldodecanoate (**5**) (3.9 g, 0.0106 mol) and pyridine (4 ml) in dichloromethane (90 ml) at 0 °C. After the mixture had been stirred for 1 h, the solvent was removed by evaporation and residue was worked up with ether in the usual way to give an oil (4.1 g) which was chromatographed on silica (80 g). Elution with ether–light petroleum (1 : 9) afforded a crude mixture of the alkenyl sulphides (**7**) and (**10**) (3.07 g, 83%) as an oil, $\nu_{max.}$ 1 740 (CO$_2$Et) and 1 720 cm$^{-1}$ (C=O); δ 7.40—7.10 (5 H, m, C$_6$H$_5$), 6.15—5.60 (1 H, m, vinyl proton), and 4.25—4.10 (2 H, m, CO$_2$C*H*$_2$CH$_3$), a portion of which (500 mg, 1.44 mmol) was treated with a boiling solution of mercury(II) chloride (1.4 g) and cadmium carbonate (2.6 g) in acetonitrile (15 ml) and water (5 ml) for 1 h. The reaction mixture was worked up with dichloromethane, and the product purified by chromatography on silica (10 g) with ether–light petroleum (1 : 1) as eluant to give ethyl 3,6-dioxododecanoate (**14**) (240 mg, 65%), identical with the previous sample.

*Ethyl* 13-*Hydroxy*-3,6-*dioxotridecanoate* (**15**).—Treatment of ethyl 13-hydroxy-3-oxo-6-phenylsulphinyltridecanoate (**6**) (0.5 g, 1.26 mmol) with trifluoroacetic anhydride (3.67 g, 0.015 mol) and pyridine (0.49 g, 6.3 mmol) in dichloromethane (10 ml) in the above manner gave, after chromatography [silica; light petroleum–ethyl acetate (4 : 1)], an oily mixture of unsaturated sulphides (**9**) and (**12**) (0.31 g, 53%) which was immediately hydrolysed by use of mercury(II) chloride and cadmium carbonate in wet acetonitrile as before to give the product (**15**) (50 mg), $\nu_{max.}$ 3 390 (OH), 1 748 (CO$_2$Et), and 1 710 cm$^{-1}$ (C=O); δ 4.18 (2 H, q, *J* 7 Hz, OC*H*$_2$CH$_3$), 3.61 (2 H, t, *J* 7 Hz, C*H*$_2$OH), 3.5 (2 H, s, COCH$_2$CO), 2.85—2.67 (4 H, m, C*H*$_2$COC*H*$_2$[CH$_2$]$_6$), 2.44 (2 H, t, *J* 7 Hz, C*H*$_2$COCH$_2$CO), and 2.04 (1 H, s, OH); *m/z* 286 (*M*$^+$).

*Ethyl* 6-*Methylthio*-3-*oxo*-6-*phenylsulphinyldodecanoate* (**19**.—A solution of 2-phenylsulphinyloct-1-ene (**1**) (1.0 g, 4.23

mmol) in THF (5 ml) was added by syringe to a solution of the dianion of ethyl 3-oxobutanoate (1.10 g, 8.46 mmol) (prepared as before) in THF (25 ml) at 0 °C under nitrogen. After 5 min, a solution of dimethyl disulphide (4.11 g, 0.043 mol) in THF (5 ml) was added, and the mixture was stirred for 10 min before being poured into saturated aqueous ammonium chloride, and then worked up with ether in the usual way. Preparative t.l.c. [ether–light petroleum (7:3)] with extraction of a band at $R_F$ 0.35 gave the product (**19**) (830 mg, 41%) as an oil, $\nu_{max.}$($CHCl_3$) 1 740 ($CO_2Et$) and 1 710 $cm^{-1}$ (C=O); δ 7.60 (5 H, m, $C_6H_5$), 4.20 (2 H, q, *J* 6 Hz, $CO_2CH_2CH_3$), 3.47 and 3.40 (2 H, 2 s, $COCH_2CO_2Et$), 2.84 (2 H, t, *J* 7 Hz, $CH_2CH_2CO$), 2.21 (2 H, t, *J* 7 Hz, $CH_2CH_2CO$), and 1.80 (3 H, s, $SCH_3$), which decomposed before it could be characterized further.

*Ethyl* 2-*Hexyl*-5-*oxocyclopent*-1-*enecarboxylate* (**21**).—A solution of ethyl 3,6-dioxododecanoate (**14**) (9.80 g, 0.038 mol) in ether (300 ml) was shaken vigorously with 8% aqueous sodium hydroxide (100 ml) for 10 min. The usual work-up with ether gave the *product* (**21**) (8.68 g, quantitative) as an oil, $\nu_{max.}$($CHCl_3$) 1 735 ($CO_2Et$), 1 705 (C=O), and 1 618 $cm^{-1}$ (C=C); $\lambda_{max.}$(EtOH) 232 nm (ε 10 400); δ 4.31 (2 H, q, *J* 8 Hz, $CO_2CH_2CH_3$), 8.74 (2 H, *J* 8 Hz, $COCH_2CH_2$), 2.66 (2 H, m, allylic protons), and 2.47 (2 H, m, allylic protons); *m/z* 238 ($M^+$) (Found: C, 70.3; H, 9.3. $C_{14}H_{22}O_3$ requires C, 70.6; H, 9.2%).

*Ethyl* 2-(7-*Hydroxyheptyl*)-5-*oxocyclopent*-1-*enecarboxylate* (**22**).—(*a*) Treatment of an ethereal solution of the dione (**15**) (1.0 g) with aqueous sodium hydroxide in the above manner gave, after chromatography (silica; ether) the *product* (**22**) (0.8 g, 85%) as an oil, $\nu_{max.}$(film) 3 350 (OH), 1 725 ($CO_2Et$), and 1 675 $cm^{-1}$ (C=C–C=O); δ 4.3 (2 H, q, *J* 6 Hz, $CO_2CH_2CH_3$), 3.62 (2 H, t, *J* 7 Hz, $CH_2OH$), 2.72 (2 H, t, *J* 7 Hz, $COCH_2CH_2$), 2.67 (2 H, m, allylic protons), 2.45 (2 H, m, allylic protons), and 1.35 (3 H, t, *J* 6 Hz, $CH_2CH_3$); *m/z* 268 ($M^+$) (Found: C, 66.9; H, 8.8. $C_{15}H_{24}O_4$ requires C, 67.1; H, 9.0%).

(*b*) A solution of 9-hydroxy-2-phenylsulphinylnon-1-ene (**2**) (3.0 g, 0.0113 mol) in THF (5 ml) was added to a solution of the lithio sodio dianion of ethyl 3-oxobutanoate (1.76 g, 1.35 mmol) in THF (50 ml) at −20 °C under nitrogen. After 15 min, dimethyl disulphide (5.3 g, 0.0563 mol) was added and the mixture was shaken vigorously for 15 min. The solvent was evaporated off to give a yellow solid which was shaken with a mixture of ether and saturated aqueous ammonium chloride. After work-up with ether the residue was dissolved in a solution of trifluoroacetic acid (4 ml) in wet benzene (25 ml). The mixture was left for 5 min, concentrated under reduced pressure, the residual oil dissolved in ether (50 ml), and the solution shaken vigorously with 8% aqueous sodium hydroxide (15 ml) for 10 min. After neutralization with dil. hydrochloric acid, the usual work-up with ether, followed by chromatography (silica; ether) gave the product (**22**) (1.0 g, 33%), identical with the previous sample.

*Ethyl* t-2-*Hexyl*-t-2- *and* -c-2-*hydroxycyclopentane*-r-1-*carboxylate* (**25**) *and* (**34**).—Sodium borohydride (3.52 g, 0.092 mol) was added to a solution of ethyl 2-hexyl-5-oxocyclopent-1-enecarboxylate (**21**) (10 g, 0.042 mol) in ethanol (300 ml) while the temperature was kept below 5 °C. When addition was complete, the mixture was stirred at 20 °C for 30 min. The solvent was evaporated off, and the usual work-up with ether gave an oil which was chromatographed on silica (200 g). Elution with ether–light petroleum (1:3) gave *ethyl* t-2-*hexyl*-c-2-*hydroxycyclopentane*-r-1-*carboxylate* (**34**) (4.72 g, 46%) as an oil, $\nu_{max.}$($CHCl_3$) 3 450 (OH) and 1 700 $cm^{-1}$ (C=O); δ 4.43 (1 H, m, C*H*OH), 4.22 (2 H, q, *J* 7 Hz, $CO_2CH_2CH_3$), 3.26 (1 H, br s, OH), 2.45—2.30 (2 H, m, C*H*$CO_2$Et and CH*H*′CHOH), and 2.10 (1 H, m, CH*H*′CHOH); *m/z* 242 ($M^+$) (Found: C, 69.6; H, 10.5. $C_{14}H_{26}O_3$ requires C, 69.4; H, 10.7%). Further elution furnished *ethyl* t-2-*hexyl*-t-2-*hydroxycyclopentane*-r-1-*carboxylate* (**25**) (3.20 g, 31%) as an oil, $\nu_{max.}$($CHCl_3$) 3 450 (OH) and 1 720 $cm^{-1}$ (C=O); δ 4.38 (1 H, m, C*H*OH), 4.20 (2 H, q, *J* 7 Hz, $CO_2CH_2CH_3$), 2.53 (1 H, br s, OH), and 2.31 (1 H, dd, *J* 6, *J*′ 10 Hz, C*H*$CO_2$Et); *m/z* 242 ($M^+$) (Found: C, 69.3; H, 10.9%).

*Ethyl* t-2- *and* c-2-*Hydroxy*-t-5-(7-*tetrahydropyran*-2-*yloxyheptyl*)*cyclopentane*-r-1-*carboxylate* (**30**) *and* (**39**).—A solution of dihydropyran (0.45 g, 5.4 mmol), picric acid (200 mg), and ethyl 2-(7-hydroxyheptyl)-5-oxocyclopent-1-enecarboxylate (**22**) (1.3 g, 4.9 mmol) in dichloromethane (15 ml) was left at room temperature for 20 h and worked up in the usual manner. The residue was reduced with sodium borohydride in the manner described above to give, after chromatography [silica; light petroleum–ethyl acetate (3:1)], the *t*-2-isomer (**30**) (0.33 g, 23%) as an oil, $\nu_{max.}$(film) 3 460 (OH) and 1 745 $cm^{-1}$ ($CO_2Et$); δ 4.56 (1 H, m, OCHO), 4.38 (1 H, m, C*H*OH), 4.18 (2 H, q, *J* 7 Hz, $COCH_2CH_3$), 3.85 (1 H, m, C*H*H′OTHP), 3.72 (1 H, m, CH*H*′OTHP), 3.47 (1 H, m, C*H*H′O), 3.35 (1 H, m, CH*H*′O), 3.17 (1 H, s, CHO*H*), and 2.33 (2 H, m, $CH_2$CHOH); *m/z* 356 ($M^+$), and the *c*-2-isomer (**39**) (0.36 g, 25%), $\nu_{max.}$(film) 3 460 (OH) and 1 744 $cm^{-1}$ ($CO_2Et$); δ 4.56 (1 H, s, OCHO), 4.37 (1 H, m, C*H*OH), 4.17 (2 H, q, *J* 7 Hz, $COCH_2CH_3$), 3.86 (1 H, m, C*H*H′OTHP), 3.72 (1 H, m, CH*H*′OTHP), 3.47 (1 H, m, C*H*H′O), 3.35 (1 H, m, CH*H*′O), and 2.33 (2 H, m, $CH_2$CHOH); *m/z* 356 ($M^+$).

r-1-*Hexyl*-t-3-*hydroxy*-t-2-(*hydroxymethyl*)*cyclopentane* (**35**).—A solution of the hydroxyester (**34**) (400 mg, 1.65 mmol) and lithium aluminium hydride (125 mg, 3.3 mmol) in ether (10 ml) was stirred for 30 min at 20 °C, and the excess of reductant was destroyed by careful dropwise addition of water. The usual work-up with ether, followed by preparative t.l.c. [silica; ether–light petroleum (3:2); extraction of the band at $R_F$ 0.4] gave the *product* (**35**) (300 mg, 92%), m.p. 38—42 °C; $\nu_{max.}$($CHCl_3$) 3 630 and 3 480 $cm^{-1}$ (OH); δ 4.43 (1 H, q, *J* 5 Hz, C*H*OH), 3.81 (2 H, m, $CH_2OH$), and 3.19 (2 H, br s, 2 OH) (Found: C, 71.8; H, 12.2. $C_{12}H_{24}O_2$ requires C, 72.0; H, 12.0%).

This compound formed a cyclic acetal on treatment with 4-nitrobenzaldehyde in the following manner. A solution of the diol (**35**) (236 mg, 0.98 mmol), 4-nitrobenzaldehyde (187 mg, 1.02 mmol), and toluene-*p*-sulphonic acid (10 mg) in benzene (30 ml) was boiled for 2 h, and the cooled solution poured onto a column of alumina (20 g). Elution with benzene gave an oil which was rechromatographed on silica (3 g). Elution with ether–light petroleum (1:9) furnished the *cyclic acetal* (331 mg, 84%), m.p. 71—73 °C (from hexane); $\nu_{max.}$($CHCl_3$) 1 350 $cm^{-1}$ (C–$NO_2$); δ 8.21 (2 H, d, *J* 4 Hz, 2 ArH), 7.65 (2 H, d, *J* 4 Hz, 2 ArH), 5.52 (1 H, s, OCHO), 4.39 (1 H, t, *J* 4 Hz, $CH_2CHOCH$), and 4.20 (2 H, d, *J* 2 Hz, $CHCH_2OCH$); *m/z* 333 ($M^+$) (Found: C, 68.2; H, 8.3; N, 4.2. $C_{19}H_{27}NO_4$ requires C, 68.5; H, 8.1; N, 4.2%).

r-1-*Hexyl*-c-3-*hydroxy*-t-2-(*hydroxymethyl*)*cyclopentane* (**26**).—Reduction of the hydroxyester (**25**) (400 mg, 1.65 mmol) with lithium aluminium hydride as before gave the *product* (**26**) (303 mg, 93%) as an oil, $\nu_{max.}$($CHCl_3$) 3 620 and 3 420 $cm^{-1}$ (OH); δ 4.07 (1 H, q, *J* 5 Hz, C*H*OH), 3.82 (1 H, dd, *J* 5, *J*′ 11 Hz, C*H*H′OH), and 3.42 (3 H, m, CH*H*′OH and 2 OH) (Found: C, 75.22; H, 11.9%). This compound did not form a cyclic acetal on treatment with 4-nitrobenzaldehyde in the manner described above.

*Ethyl* t-2-*Hexyl*-t-5-(*tetrahydropyran*-2-*yloxy*)*cyclopentane*-r-1-*carboxylate* (**27**).—A solution of the hydroxyester (**25**) (2.5 g, 9.7 mmol), 2,3-dihydropyran (1.04 g, 0.0012 mol), and picric acid (150 mg) in dichloromethane (80 ml), was kept for 18 h at

20 °C and was then evaporated and the residue worked up with ether in the usual manner to give, after chromatography [silica; ether–light petroleum (17:3)], the *product* (**27**) (2.51 g, 75%) as an oil, $\nu_{max.}$(CHCl$_3$) 1 730 cm$^{-1}$ ($CO_2$Et); δ 4.65 (1 H, m, OCHO), 4.40 (1 H, m, C*H*OTHP), 4.18 (2 H, q, *J* 6 Hz, $CO_2CH_2CH_3$), and 2.42 (1 H, m, C*H*$CO_2$Et); *m/z* 326 ($M^+$) (Found: C, 69.55; H, 10.7. $C_{19}H_{34}O_4$ requires C, 69.9; H, 10.4%).

*Ethyl* t-2-*Hexyl*-c-5-(*tetrahydropyran*-2-*yloxy*)*cyclopentane*-r-1-*carboxylate* (**36**).—Prepared in the above manner from the hydroxyester (**34**) (76%), this *compound* had $\nu_{max.}$(CHCl$_3$) 1 730 cm$^{-1}$ ($CO_2$Et); δ 4.73 and 4.65 (1 H, m, OCHO), 4.51 and 4.41 (1 H, m, C*H*OTHP), and 4.17 (2 H, m, $CO_2CH_2CH_3$); *m/z* 326 ($M^+$) (Found: C, 70.1; H, 10.3%).

*The Tetrahydropyranyl Ethers* (**31**) *and* (**40**).—These were prepared in the above manner from the hydroxyesters (**30**) and (**39**) respectively. *Compound* (**31**) (96%) had $\nu_{max.}$(film) 1 740 cm$^{-1}$ ($CO_2$Et); δ 4.57 (2 H, m, 2 OCHO), 4.36 (1 H, m, C*H*OTHP), 4.14 (2 H, q, *J* 7 Hz, $CO_2CH_2CH_3$), 3.85 (3 H, m, C*H*H′OTHP and $CH_2$CHOTHP), 3.71 (1 H, m, CH*H*′OTHP), and 2.38 (1 H, m, C*H*$CO_2$Et); *m/z* 440 ($M^+$) (Found: C, 68.4; H, 9.9. $C_{25}H_{44}O_6$ requires C, 68.2; H, 10.1%). *Compound* (**40**) (89%) had $\nu_{max.}$(film) 1 745 cm$^{-1}$ ($CO_2$Et); δ 4.57 (2 H, m, 2 OCHO), 4.36 (1 H, m, C*H*OTHP), 4.13 (2 H, q, *J* 7 Hz, $CO_2CH_2CH_3$), 3.85 (3 H, m, C*H*H′OTHP and $CH_2$CHOTHP), 3.71 (1 H, m, C*H*H′OTHP), 3.47 (2 H, m), 3.35 (2 H, m), and 2.46—2.3 (1 H, m, CHC$O_2$Et); *m z* 440 ($M^+$) (Found: C, 67.8; H, 9.9%).

r-1-*Hexyl*-t-2-*hydroxymethyl*-c-3- *and* -t-3-(*tetrahydropyran*-2-*yloxy*)*cyclopentane*, (**28**) *and* (**37**).—A solution of the ester (**27**) (2.2 g, 67 mmol) in ether (5 ml) was added slowly to a cooled, stirred suspension of lithium aluminium hydride (0.5 g, 0.013 mol) in ether (35 ml). After the mixture had been stirred for 30 min at room temperature the usual work-up with ether gave r-1-*hexyl*-t-2-*hydroxymethyl*-c-3-(*tetrahydropyran*-2-*yloxy*)-*cyclopentane* (**28**) (1.92 g, 99%) as an oil, $\nu_{max.}$(CHCl$_3$) 3 620 and 3 450 cm$^{-1}$ (OH); δ 4.75 and 4.58 (1 H, m, OCHO), 4.17 (1 H, q, *J* 6 Hz, C*H*OTHP), 3.80 (2 H, m, $CH_2O$), and 3.28 (2 H, m, $CH_2$OH); *m/z* 284 ($M^+$) (Found: C, 71.5; H, 11.4. $C_{17}H_{32}O_3$ requires C, 71.8; H, 11.3%). The *isomer* (**37**) (99%), $\nu_{max.}$(CHCl$_3$) 3 460 cm$^{-1}$ (OH); δ 4.63 and 4.54 (1 H, both m, OCHO in diastereoisomeric THP ethers), 4.46 and 4.36 (1 H, both q, *J* 6 Hz, C*H*OTHP in diastereoisomeric THP ethers), 3.72 (2 H, m, $CH_2$OH), and 2.83 (1 H, br s, OH); *m/z* 284 ($M^+$) (Found: C, 71.6; H, 11.25%) was obtained by reduction of the ester (**36**) in the same way.

t-2-*Hydroxymethyl*-r-1-(*tetrahydropyran*-2-*yloxy*)-c-3- *and* tc-2-*Hydroxymethyl*-r-1-(*tetrahydropyran*-2-*yloxy*)-t-3-[7-(*tetrahydropyran*-2-*yloxy*)*heptyl*]*cyclopentane* (**32**) *and* (**41**).—Reduction of the ester (**31**) (130 mg) with lithium aluminium hydride in the above manner gave the t-2-*hydroxymethyl*-r-1-*tetrahydropyranyloxy isomer* (**32**) (70 mg, 60%) as an oil, $\nu_{max.}$(film) 3 455 cm$^{-1}$ (OH); δ 4.57 (2 H, m, 2 OCHO), 3.87 (3 H, m, $CH_2$CHOTHP and C*H*H′OTHP), 3.71 (1 H, m, CH*H*′OTHP), and 3.53 (2 H, t, $CH_2$OH); *m/z* 398 ($M^+$) (Found: C, 69.5; H, 10.8. $C_{23}H_{42}O_5$ requires C, 69.3; H, 10.6%). Reduction of the isomeric ester (**40**) (890 mg) in the same way gave the c-2-*hydroxymethyl*-r-1-*tetrahydropyranyloxy isomer* (**41**) (450 mg, 56%) as an oil, $\nu_{max.}$ 3 470 cm$^{-1}$ (OH); δ 4.57 (2 H, m, 2 OCHO), 3.87 (3 H, m, $CH_2$CHOTHP and C*H*H′OTHP), 3.70 (1 H, m, CH*H*′OTHP), and 3.51 (2 H, t, $CH_2$OH); *m/z* 398 ($M^+$) (Found: C, 69.6; H, 10.9%).

t-2-*Formyl*-r-1-*hexyl*-c-3- *and* -t-3-(*tetrahydropyran*-2-*yloxy*)-*cyclopentane*, (**29**) *and* (**38**), *and Their Analogues* (**33**) *and* (**42**).—A solution of the hydroxymethyl compound (**28**) (1.7 g, 6 mmol) in dichloromethane (50 ml) was added to a solution of dipyridine chromium trioxide[37] (9.73 g, 36 mmol) in dichloromethane (150 ml) at 20 °C. After 30 min the organic phase was decanted off and the residue was washed with dichloromethane. The combined dichloromethane extracts were washed with water, dried ($MgSO_4$), and evaporated, to furnish the *aldehyde* (**29**) (1.69 g, 99%), $\nu_{max.}$(CHCl$_3$) 1 720 cm$^{-1}$ (CHO); δ 9.82 and 9.69 (1 H, both d, *J* 2 Hz, CHC*H*O in diastereoisomers owing to presence of THP ether), 4.65 (1 H, m, OCHO), 4.44 (1 H, q, *J* 5 Hz, C*H*OTHP), and 2.58 and 2.46 (1 H, both m, C*H*CHO in diastereoisomeric THP ethers); *m/z* 282 ($M^+$) (Found: C, 72.5; H, 10.4. $C_{17}H_{30}O_3$ requires C, 72.3; H, 10.6%).

Oxidation of the isomeric hydroxymethyl compound (**37**) in the same way gave the *aldehyde* (**38**) (70%), $\nu_{max.}$(CHCl$_3$) 1 720 cm$^{-1}$ (CHO); δ 9.80 and 9.67 (1 H, both d, *J* 2 Hz, CHC*H*O in diastereoisomers owing to presence of THP ether), 4.60 (1 H, m, OCHO), 4.47 (1 H, q, *J* 8 Hz, C*H*OTHP), and 2.45 (1 H, m, C*H*CHO); *m/z 282* ($M^+$) (Found: C, 72.5; H, 10.6%).

The alcohols (**32**) and (**41**) were oxidised in the above manner to give respectively the aldehyde (**33**) (95%), $\nu_{max.}$(film) 1 728 cm$^{-1}$ (CHO); δ 9.72 (1 H, d, CHO), and the aldehyde (**42**) (97%), $\nu_{max.}$(film) 1 727 cm$^{-1}$; δ 9.71 (1 H, d, CHO), which were used immediately in reactions with 1-tributylphosphoranylideneheptan-3-one.

(E)-15-*Oxo*-11α-(*tetrahydropyran*-2-*yloxy*)-1-*norprost*-13-*ene* (**43**).—A solution of the aldehyde (**33**) (1.49 g, 5.3 mmol) and 1-tributylphosphoranylideneheptan-3-one[14] (2.16 g, 6.9 mmol) in ether (20 ml) was kept for 17 h at 20 °C, after which the solvent was removed by evaporation, and the residue was chromatographed [silica; ether–light petroleum (1:9)] to furnish the *product* (**43**) (1.66 g, 83%) as an oil, $\nu_{max.}$(CHCl$_3$) 1 668 and 1 662 cm$^{-1}$ (C=C–C=O); δ 6.76 and 6.72 (1 H, both dd, *J* 7, *J*′ 15 Hz, C*H*=CHCO in diastereoisomers owing to presence of THP ether), 6.17 and 6.13 (1 H, both d, *J* 15 Hz, CH=C*H*CO in diastereoisomers), 4.65 and 4.55 (1 H, m, OCHO in diastereoisomers), 4.02 (1 H, q, *J* 6 Hz, C*H*OTHP), 2.54 (2 H, t, *J* 6 Hz, $CH_2$CO), and 2.22 (1 H, m, allylic proton) (Found: C, 76.3; H, 11.25. $C_{24}H_{42}O_3$ requires C, 76.2; H, 11.1%).

15-*Oxo*-1,11α- *and* -1,11β-*bis*(*tetrahydropyran*-2-*yloxy*)*prost*-13-*ene* (**44**) *and* (**45**).—The aldehyde (**33**) (0.2 g) was treated with 1-tributylphosphoranylideneheptan-3-one in the above manner to give the *product* (**44**) (0.15 g, 60%), $\nu_{max.}$ 1 680 and 1 630 cm$^{-1}$ (C=C–C=O); δ 6.73 (1 H, m, C*H*=CHCO), 6.13 (1 H, m, CH=C*H*CO), 4.55 (2 H, m 2 OCHO), 2.51 (2 H, t, *J* 7 Hz, $CH_2$CO), 2.22 (1 H, m, allylic proton), and 0.86 (3 H, t, $CH_2CH_3$); *m/z* 492 ($M^+$) (Found: C, 73.4; H, 10.9. $C_{30}H_{52}O_5$ requires C, 73.1; H, 10.6%). Similar treatment of the aldehyde (**42**) (0.3 g) gave the *enone* (**45**) (0.2 g, 54%), $\nu_{max.}$(film) 1 680 and 1 630 cm$^{-1}$ (C=C–C=O); δ 6.76 (1 H, m, C*H*=CHCO), 6.13 (1 H, m, CH=C*H*CO), 4.56 (2 H, m, 2 OCHO), 2.53 (2 H, t, $CH_2$CO), 2.22 (1 H, m, allylic proton), and 0.86 (3 H, t, $CH_2CH_3$); *m/z* 492 ($M^+$) (Found: C, 72.9; H, 10.5%).

11α,15α- *and* 11α,15β-*Dihydroxy*-1-*norprost*-13-*ene* (**46**) *and* (**47**).—Sodium borohydride (480 mg, 0.0125 mol) was added to a solution of the enone (**43**) (1.2 g, 3.1 mmol) in ethanol (50 ml) at 10 °C, and after being stirred for 3 h the mixture was worked up with ether. The oily product was dissolved in methanol (100 ml) containing dil. hydrochloric acid (0.5 ml), and after being left overnight the mixture was worked up with ether, and the product was chromatographed [silica; ether–light petroleum (7:3)] to give 11α,15β-*dihydroxy*-1-*norprost*-13-*ene* (**47**) (496 mg, 52%), $\nu_{max.}$(CHCl$_3$) 3 610 and 3 410 cm$^{-1}$ (OH); δ 5.67 (2 H, m, vinyl protons), 4.10 (1 H, q, *J* 6 Hz, CH=CHC*H*OH), and 3.88 (1 H, m, C*H*OH) (Found: C, 76.9; H, 12.3. $C_{19}H_{36}O_2$ requires C, 77.0; H, 12.2%). Further elution gave 11α,15α-

*dihydroxy*-1-*norprost*-13-*ene* (**46**) (293 mg, 31%), $\nu_{max.}$($CHCl_3$) 3 610 and 3 410 $cm^{-1}$ (OH); δ 5.51 (1 H, dd, *J* 6, *J'* 15 Hz, CH=C*H*CHOH), 5.41 (1 H, dd, *J* 6, *J'* 15 Hz, C*H*=CHCHOH), 4.02 (1 H, q, *J* 6 Hz, CH=CHC*H*OH), and 3.80 (1 H, q, *J* 7 Hz, C*H*OH) (Found: C, 76.9; H, 12.1%).

11β,15α- *and* 11β,15β-*Dihydroxy*-1-*norprost*-13-*ene* (**48**) *and* (**49**).—A solution of the aldehyde (**38**) (1.49 g) and 1-tributylphosphoranylideneheptan-2-one (2.16 g, 6.9 mmol) in ether (20 ml) was kept for 18 h at room temperature, and the solvent removed by evaporation. The residue was dissolved in ether–light petroleum (9:1) and filtered through silica (25 g). The filtrate was evaporated, and the residual oil (1.42 g) was dissolved in ethanol (50 ml) and treated with sodium borohydride (480 mg, 0.0125 mol) at 10 °C. After the mixture had been stirred at room temperature for 3 h, the usual work-up with ether gave an oil which was dissolved in methanol (100 ml) containing dil. hydrochloric acid (0.5 ml). After 18 h at room temperature the mixture was worked up with ether, and the product was subjected to preparative high performance liquid chromatography (h.p.l.c.) on a 25 cm Spherisorb column eluted with a mixture of light petroleum (b.p. 60—80 °C) and ethyl acetate (3 : 1) to give 11β,15α-*dihydroxy*-1-*norprost*-13-*ene* (**48**) $\nu_{max.}$($CHCl_3$) 3 600 and 3 400 $cm^{-1}$ (OH); δ 5.73, (1 H, dd, *J* 6, *J'* 15 Hz, CH=C*H*CHOH), 5.59 (1 H, dd, *J* 6, *J'* 15 Hz, C*H*=CHCHOH), and 4.13 (2 H, m, 2 C*H*OH) (Found: C, 77.25; H, 12.0. $C_{19}H_{36}O_2$ requires C, 77.0; H, 12.2%), and 11β,15β-*dihydroxy*-1-*norprost*-13-*ene* (**49**), $\nu_{max.}$($CHCl_3$) 3 600 and 3 400 $cm^{-1}$ (OH); δ 5.70 (1 H, dd, *J* 8, *J'* 15 Hz, CH=C*H*CHOH), 5.53 (1 H, dd, *J* 8, *J'* 15 Hz, C*H*=CHCHOH), 4.19 (1 H, m, CH=CHC*H*OH), and 4.11 (1 H, m, C*H*OH) (Found: C, 77.25; H, 12.0%).

*Preparation of the Allylic Alcohols* (**50**)—(**53**).—Treatment of a solution of the enone (**44**) (110 mg, 0.22 mmol) in ethanol (5 ml) with sodium borohydride (17 mg, 0.45 mmol) for 1 h, and work-up with ether gave, after chromatography, 15α-*hydroxy*-1,11α-*bis*(*tetrahydropyran*-2-*yloxy*)*prost*-13-*ene* (**50**) (32 mg, 29%), $\nu_{max.}$(film) 3 450 $cm^{-1}$ (OH); δ 5.82 (1 H, m, CH=C*H*CHOH), 5.48 (1 H, m, C*H*=CHCHOH), 4.55 (2 H, m, 2 OCHO), 3.83 (3 H, m, C$H_2$CHOTHP and CHH'OTHP), 3.7 (1 H, m, CH*H'*OTHP), 3.45 (2 H, $CH_2O$), and 0.85 (3 H, t, $CH_2CH_3$); *m/z* 494 ($M^+$) (Found: C, 72.6; H, 11.1. $C_{30}H_{54}O_5$ requires C, 72.8; H, 11.0%), and 15β-*hydroxy*-1,11α-*bis*(*tetrahydropyran*-2-*yloxy*)*prost*-13-*ene* (**51**) (46 mg, 42%), $\nu_{max.}$(film) 3 450 $cm^{-1}$ (OH); δ 5.82 (1 H, m, C*H*=CHCHOH), 5.49 (1 H, m, CH=C*H*CHOH), 4.56 (2 H, m, 2 OCHO), 3.84 (3 H, m, C$H_2$CHOTHP and CHH'OTHP), 3.7 (1 H, m, CH*H'*OTHP), 3.45 (2 H, m, $CH_2O$), 3.35 (2 H, m, $CH_2O$), and 0.85 (3 H, t, $CH_2CH_3$); *m/z* 494 ($M^+$) (Found: C, 72.5; H, 11.3%).

Reduction of the enone (**45**) (190 mg) in the same way gave 15β-*hydroxy*-1,11β-*bis*(*tetrahydropyran*-2-*yloxy*)*prost*-13-*ene* (**53**) (56 mg), $\nu_{max.}$(film) 3 450 $cm^{-1}$ (OH); δ 5.81 (1 H, m, CH=C*H*CHOH), 5.47 (1 H, m, C*H*=CHCHOH), 4.55 (2 H, m, 2 OCHO), 3.83 (3 H, m, C$H_2$CHOTHP and CHH'OTHP), 3.69 (1 H, m, CH*H'*OTHP), 3.45 (2 H, m, $CH_2O$), 3.34 (2 H, m, $CH_2O$), and 0.85 (3 H, t, $CH_2CH_3$); *m/z* ($M^+$) 494 (Found: C, 72.6; H, 11.1%), and 15α-*hydroxy*-1,11β-*bis*(*tetrahydropyran*-2-*yloxy*)*prost*-13-*ene* (**52**) (83 mg), $\nu_{max.}$(film) 3 450 $cm^{-1}$ (OH); δ 5.81 (1 H, m, CH=C*H*CHOH), 5.47 (1 H, m, C*H*=CHCHOH), 4.56 (2 H, m, 2 OCHO), 3.84 (3 H, m, C$H_2$CHOTHP and CHH'OTHP), 3.7 (1 H, m, CH*H'*OTHP), 3.45 (2 H, m, $CH_2O$), 3.36 (2 H, m, $CH_2O$), and 0.86 (3 H, t, $CH_2CH_3$); *m/z* 494 ($M^+$) (Found: C, 72.5; H, 11.3%).

1,11α,15α-*Trihydroxyprost*-13-*ene* (**54**).—A solution of compound (**50**) (32 mg, 65 μmol) in methanol (2 ml) containing dil. hydrochloric acid (0.01 ml) was left at room temperature overnight, the solvent was evaporated off, and the residue worked up with ether in the usual way to give, after chromatography (silica; ether), the *product* (**54**) (10 mg, 48%), δ 5.5 (1 H, dd, $J_{AB}$ 15.5, $J_{AX}$ 6.5 Hz, CH=C*H*CHOH), 5.46 (1 H, dd, $J_{AB}$ 15.5, $J_{BX}$ 8.5 Hz, C*H*=CHCHOH), 4.08 (1 H, q, *J* 6.5 Hz, CH=CHC*H*OH), 3.86 (1 H, t, *J* 7.5 Hz, homoallylic proton), and 3.63 (2 H, t, *J* 7 Hz, C$H_2$OH) (Found: $M^+$, 326.2813. $C_{20}H_{38}O_3$ requires *M*, 326.2821).

1,11α,15β-*Trihydroxyprost*-13-*ene* (**55**).—Hydrolysis of the acetal (**51**) (46 mg) in the above manner gave the *product* (**55**) (17 mg, 57%), δ 5.59 (1 H, dd, $J_{AB}$ 15.5, $J_{AX}$ 6 Hz, CH=C*H*CHOH), 5.50 (1 H, dd, $J_{AB}$ 15.5, $J_{BX}$ 8.5 Hz, C*H*=CHCHOH), 4.10 (1 H, q, *J* 6 Hz, CH=CHC*H*OH), 3.86 (1 H, q, *J* 8 Hz, homoallylic proton), 3.63 (2 H, dt, $J_{CD}$ 7, $J_{CY}$ 2.5 Hz, C$H_2$OH), 2.89 (1 H, m, $CH_2OH$) (Found: $M^+$ 326.2806).

2-*Phenylsulphinyloct*-1-*en*-3-*one* (**56**).—Jones reagent[38] (2.88 ml, 0.0115 mol) was added quickly to a stirred solution of 2-phenylsulphinyloct-1-en-3-ol[13] (2.0 g, 7.9 mmol) in acetone (100 ml) at 0 °C. After the mixture had been stirred for 10 min the acetone was decanted off, the residue washed with acetone, and the combined acetone extracts filtered through Hyflo Supercel. The solvent was evaporated off, and the residue worked up with ether in the usual manner to give an oil which was chromatographed [silica; ether–light petroleum (1 : 1)] to give the *product* (**56**) (1.60 g, 80%), $\nu_{max.}$(film) 1 674 (C=O) and 1 046 $cm^{-1}$ (S=O); δ 7.59 (5 H, m, $C_6H_5$), 6.86 (1 H, d, *J* 2.4 Hz, CH=C *cis* to SO), 6.68 (1 H, d, *J* 2.4 Hz, CH=C *trans* to SO), 2.62 (2 H, m, $CH_2CO$), 1.47 (2 H, qn, *J* 7.5 Hz, C$H_2CH_2CO$), 1.15 (4 H, m, C$H_2$C$H_2CH_3$), and 0.80 (3 H, t, *J* 7 Hz, $CH_2CH_3$); *m/z* 250 ($M^+$) (Found: C, 67.3; H, 7.2; S, 13.0. $C_{14}H_{18}O_2S$ requires C, 67.2; H, 7.2; S, 12.8%).

*Methyl* 2-*Oxo*-1-(3-*oxo*-2-*phenylsulphinyloctyl*)*cyclopentanecarboxylate* (**57**).—Potassium carbonate (269 mg, 1.95 mmol) was added to a stirred solution of methyl 2-oxocyclopentanecarboxylate (554 mg, 3.9 mmol) and 2-phenylsulphinyloct-1-en-3-one (**56**) (980 mg, 3.9 mmol) in wet ether (30 ml) at room temperature. After 15 min the mixture was worked up with ether to give the *product* (**57**) (1.53 g, 99%) as an oil, $\nu_{max.}$($CHCl_3$) 1 745 ($CO_2Me$), 1 723 (C=O), and 1 040 $cm^{-1}$ (S=O); δ (5 H, m, $C_6H_5$), 4.19 (1 H, m, C*H*SOPh), 3.60 (3 H, s, $CO_2CH_3$), 2.34 (6 H, m), 1.95 (2 H, m), 1.43 (8 H, m), and 0.85 (3 H, t, *J* 7 Hz, $CH_2CH_3$); *m/z* 374 ($M^+$) (Found: C, 63.2; H, 7.2; S, 8.4. $C_{28}H_{20}O_5S$ requires C, 63.5; H, 7.3; S, 8.4%).

*Reaction of* 2-*Phenylsulphinyloct*-1-*en*-3-*one* (**56**) *with Ethyl* 3-*Oxobutanoate*.—A solution of 2-phenylsulphinyloct-1-en-3-one (**56**) (265 mg, 1.1 mmol) and ethyl 3-oxobutanoate (143 mg, 1.1 mmol) in wet ether (20 ml) containing potassium carbonate (151 mg, 1.1 mmol) was stirred for 1 h at 20 °C, and then worked up with ether to give an oil which was chromatographed on silica (25 g). Elution with ether–light petroleum (3:2) gave *ethyl* 2-*acetyl*-5-*oxo*-2-(3-*oxo*-2-*phenylsulphinyloctyl*)-4-*phenylsulphinyldecanoate* (**62**) (95 mg, 23%) as an oil, $\nu_{max.}$($CHCl_3$) 1 765 and 1 047 $cm^{-1}$; δ 7.61 (10 H, m, 2 $C_6H_5$), 4.03 (4 H, m, O$CH_2CH_3$ and 2 C*H*SOPh), 2.30 (8 H, m), 1.98 (3 H, $COCH_3$), 1.34 (15 H, m), and 0.92 (6 H, br t, 2 $CH_2CH_3$) (Found: C, 64.8; H, 6.9; S, 9.9. $C_{34}H_{46}O_7S_2$ requires C, 64.8; H, 7.3; S, 10.1%). Further elution gave *ethyl* 2-*acetyl*-5-*oxo*-4-*phenylsulphinyldecanoate* (**59**) (160 mg, 39%) as an oil, $\nu_{max.}$ 1 737 ($CO_2Et$), 1 712 (C=O), and 1 034 $cm^{-1}$ (S=O); δ 7.57 (5 H, m, $C_6H_5$), 4.17 (2 H, q, *J* 7 Hz, O$CH_2CH_3$), 3.82 (1 H, m, C*H*SOPh), 2.35 (3 H, m), 2.20 (3 H, $CH_3CO$), 2.04 (1 H, m), 1.30 (6 H, m), 1.24 (3 H, t, *J* 7 Hz, $OCH_2CH_3$), and 0.84 (3 H, m, $CH_2CH_3$); *m/z* 381 ($M^+$) (Found: C, 63.05; H, 7.3; S, 8.6. $C_{20}H_{28}O_5S$ requires C, 63.2; H, 7.4; S, 8.4%).

*Reaction of* 2-*Phenylsulphinyloct*-1-*en*-3-*one* (**56**) *with Dimethyl Malonate*.—The diester (318 mg, 2.41 mmol) reacted with the unsaturated sulphoxide (602 mg, 2.41 mmol) under the above conditions (after 3.5 h) to give dimethyl bis(3-oxo-2-phenylsulphinyloctyl)malonate (**61**) (131 mg, 14%), m.p. 96—98 °C; $\nu_{max.}$($CHCl_3$) 1 780 and 1 040 $cm^{-1}$; δ 7.62 (10 H, m, 2 $C_6H_5$), 4.02 (2 H, m, 2 C*H*SOPh), 3.43 (6 H, 2 s, $CO_2CH_3$), 2.25 (8 H, m), 1.31 (12 H, m), 0.86 (3 H, t, *J* 7 Hz, $CH_2CH_3$), and *dimethyl* (3-*oxo*-2-*phenylsulphinyloctyl*)*malonate* (**58**) (418 mg, 45%) as an oil, $\nu_{max.}$($CHCl_3$) 1 732 ($CO_2Me$), 1 710 (C=O), and 1 040 $cm^{-1}$ (S=O); δ 7.57 (5 H, m, $C_6H_5$), 5.96 (1 H, dt, *J* 7 Hz, C*H*SOPh), 3.70 (6 H, s, 2 $CO_2CH_3$), 3.50 (1 H, q, *J* 7 Hz, C*H*$CO_2$Me), 2.36 (4 H, m), 1.32 (6 H, m), and 0.86 (3 H, m, $CH_2CH_3$); *m*/*z* 381 ($M^+$) (Found: C, 59.9; H, 6.9; S, 8.65. $C_{19}H_{26}O_6S$ requires C, 59.7; H, 6.8; S, 8.4%).

*Thermolysis of the Adducts* (**57**), (**58**), *and* (**61**).—(*a*) A solution of the adduct (**57**) (1.52 g, 3.88 mmol) in toluene (120 ml) was boiled for 30 min. The solvent was removed by evaporation, and the residue was chromatographed [silica; ether–light petroleum (1:3)] to give *methyl* 2-*oxo*-1-(3-*oxo*-*oct*-1-*enyl*)*cyclopentanecarboxylate* (**60**) (839 mg, 81%), $\nu_{max.}$($CHCl_3$) 1 735, 1 675, and 1 613 $cm^{-1}$; δ 6.94 (1 H, d, *J* 16 Hz, C*H*=CH–CO), 6.16 (1 H, d, *J* 16 Hz, CH=C*H*–CO), 3.74 (3 H, s, $CO_2CH_3$), 2.58 (2 H, t, *J* 7 Hz, $COCH_2$), 2.32 (6 H, m), 1.60 (2 H, qn, *J* 7 Hz), 1.30 (4 H, m), and 0.88 (3 H, t, *J* 7 Hz, $CH_2CH_3$); *m*/*z* 266 ($M^+$) (Found: C, 67.9; H, 8.3. $C_{15}H_{22}O_4$ requires C, 67.7; H, 8.3%).

(*b*) The adduct (**58**) (300 mg) after 15 min in boiling xylene gave *methyl* 2-*oxo*-6-*pentyl*-2H-*pyran*-3-*carboxylate* (**64**) (98 mg, 55%) as an oil, δ 8.21 (1 H, d, *J* 7 Hz, HC=C), 6.20 (1 H, d, *J* 7 Hz, C–CH), 3.9 (3 H, s, $OCH_3$), 2.57 (2 H, t, *J* 7 Hz, C=C$CH_2$), 1.71 (2 H, m), 1.35 (7 H, m), and 0.90 (3 H, t, *J* 7 Hz, $CH_2CH_3$); $\delta_C$ 172.91 (s, C=O), 164.11 (s, C=O), 150.16 (d, C=CH), 113.70 (s, C=C), 102.96 (d, HC=C), 53.57 (s, C=C), 52.54 (q, $OCH_3$), 34.28 (t, $CH_2$), 31.12 (m, $CH_2$), 26.45 (m, $CH_2$), 22.27 (m, $CH_2$), and 13.83 p.p.m. (q, $CH_3$) (Found: C, 64.1; H, 7.40 $C_{12}H_{16}O_4$ requires C, 64.3; H, 7.1%).

(*c*) The adduct (**61**) (94 mg) after 5 min in boiling xylene gave *dimethyl bis*(3-*oxo*-*oct*-1-*enyl*)*malonate* (**63**) (48 mg, 86%) as an oil, $\nu_{max.}$($CHCl_3$) 1 742 ($CO_2Me$), 1 704, 1 683, and 1 627 $cm^{-1}$ (C=C–C=O); δ 7.1 (2 H, d, *J* 16 Hz, C*H*=CHCO), 6.1 (2 H, d, *J* 16 Hz, CH=C*H*CO), 3.82 (6 H, s, 2 $CO_2CH_3$), 2.57 (4 H, t, *J* 9 Hz, 2 $CH_2CO$), 1.61 (4 H, qn, *J* 9 Hz, 2 $CH_2CH_2CO$), 1.3 (8 H, m), and 0.88 (6 H, t, *J* 7 Hz, 2 $CH_2CH_3$) (Found: C, 66.2; H, 8.3. $C_{21}H_{32}O_6$ requires C, 66.3; H, 8.3%).

*Ethyl* trans-2-*Hexyl*-5-*oxocyclopentanecarboxylate* (**65**).—(*a*) Sodium cyanoborohydride (32 mg, 0.51 mmol) was added to a stirred solution of ethyl 2-hexyl-5-oxocyclopent-1-enecarboxylate (**21**) (100 mg, 0.42 mmol) in methanol (10 ml) maintained at pH 4 by occasional addition of dil. hydrochloric acid. After 80 min, the solvent was evaporated off and the residue was worked up with ether to give an oil. Chromatography [silica; ether–light petroleum (1:3)] gave the *product* (**65**) (55 mg, 54%) as an oil, $\nu_{max.}$($CHCl_3$) 1 752 ($CO_2Et$) and 1 725 $cm^{-1}$ (C=O); δ 4.22 (2 H, q, *J* 7 Hz, $CO_2CH_2CH_3$), 2.82 (1 H, d, *J* 12 Hz, C*H*$CO_2$Et), 2.57 (1 H, m, C*H*C$HCO_2$Et), and 2.3 (2 H, m); *m*/*z* 240 ($M^+$) (Found: C, 70.2; H, 10.0. $C_{14}H_{24}O_3$ requires C, 70.0; H, 10.0%).

(*b*) A mixture (10.77 g, 0.044 mol) of the hydroxyesters (**25**) and (**34**) in acetone (360 ml) was treated with Jones reagent[38] (18.4 ml). After the mixture had been stirred for 30 min at 20 °C the usual work-up gave the product (**65**) (8.40 g, 78%), identical with the previous sample.

*Ethyl* trans-2-(7-*Hydroxyheptyl*)-5-*oxocyclopentanecarboxylate* (**66**).—Ethyl 2-(7-hydroxyheptyl)-5-oxocyclopent-1-enecarboxylate (**22**) (0.6 g, 2.22 mmol) dissolved in methanol (10 ml) was reduced by sodium borohydride (0.17 g, 2.67 mmol) in the manner described above to give the *product* (**66**) (0.41 g, 68%) as an oil, $\nu_{max.}$ 3 400 (OH), 1 765 ($CO_2Et$), and 1 730 $cm^{-1}$ (C=O); δ 4.19 (2 H, q, *J* 7 Hz, O$CH_2CH_3$), 3.58 (2 H, t, *J* 7 Hz, $CH_2OH$), 2.78 (1 H, d, *J* 10 Hz, C*H*$CO_2$Et), and 2.58 (2 H, t, $CH_2CO$); *m*/*z* 270 ($M^+$) (Found: C, 66.5; H, 9.8. $C_{15}H_{26}O_4$ requires C, 66.6; H, 9.7%).

12α- *and* 12β-*Ethoxycarbonyl*-11,15-*dioxo*-1-*norprost*-13-*ene* (**69**) *and* (**70**).—Potassium carbonate (119 mg, 0.8 mmol) was added to a stirred solution of ethyl *trans*-2-hexyl-5-oxocyclopentanecarboxylate (**65**) (2.06 g, 8.5 mmol) and 2-phenylsulphinyloct-1-en-3-one (**56**) (2.36 g, 9.4 mmol) in wet ether (40 ml). After 45 min, the mixture was worked up with ether to give an oil which was dissolved in toluene (60 ml) containing trimethyl phosphite (2.4 g, 0.019 mol). The solution was boiled for 30 min under nitrogen, and the solvent removed by evaporation. Chromatography [silica; ether–light petroleum (1:9)] of the residue afforded a mixture of the *dioxoesters* (**69**) and (**70**) (2.4 g, 89%), $\nu_{max.}$($CHCl_3$) 1 755 ($CO_2Et$), 1 730 (C=O), and 1 670 and 1 620 $cm^{-1}$ (C=C–C=O); δ 7.05 and 6.92 (relative intensity 8:1, 1 H, both d, *J* 17 Hz, C*H*=CHCO in 12α- and 12β-isomer respectively), 6.19 and 6.07 (relative intensity 8 : 1, 1 H, both d, *J* 17 Hz, CH=C*H*CO in 12α- and 12β-isomer respectively), 4.21 (2 H, m, $CO_2CH_2CH_3$), and 2.6 (2 H, m, $CH_2CO$); *m*/*z* 364 ($M^+$) (Found: C, 72.6; H, 9.9. $C_{22}H_{36}O_4$ requires C, 72.5; H, 9.9%).

12α- *and* 12β-*Ethoxycarbonyl*-1-*hydroxy*-11,15-*dioxoprost*-13-*ene* (**71**) *and* (**72**).—Treatment of the oxoester (**66**) (260 mg, 0.96 mmol) with 2-phenylsulphinyloct-1-en-3-one (**56**) (270 mg, 1.06 mmol) in the manner described above, followed by thermolysis and chromatography, gave a mixture (330 mg, 87%) of the *dioxohydroxyesters* (**71**) and (**72**), $\nu_{max.}$(film) 3 440 (OH), 1 750 ($CO_2Et$), 1 725 (C=O), and 1 675 and 1 620 $cm^{-1}$ (C=C–C=O); δ 7.1 and 7.02 (relative intensity 8:1, 1 H, both d, *J* 17 Hz, C*H*=CHCO in 12α- and 12β-isomer respectively), 6.22 and 6.16 (relative intensity 8:1, 1 H, both d, *J* 17 Hz, CH=C*H*CO in 12α- and 12β-isomer respectively), 4.19 (2 H, m, $CO_2CH_2CH_3$), 3.59 (2 H, t, *J* 7 Hz, $CH_2OH$), 3.00 (1 H, br s, OH), and 2.60 (2 H, m, $CH_2CO$); $\delta_C$ 212.31 (C-15), 200.54 and 199.45 (relative intensity 11:3, C-11 in the 12α- and 12β-isomer respectively), 170.12 and 168.48 (relative intensity 1:10, ester carbonyl C in the 12α- and 12β-isomer respectively), 142.42 and 137.78 (relative intensity 54:10, C-13 in the 12α- and 12β-isomer), and 132.17 and 130.68 p.p.m. (relative intensity 13:57, C-14 in the 12α- and 12β-isomer); *m*/*z* 394 ($M^+$) (Found: C, 69.7; H, 9.5. $C_{23}H_{38}O_5$ requires C, 70.0; H, 9.7%).

12α-*Ethoxycarbonyl*-15α-*hydroxy*-11-*oxo*-1-*norprost*-13-*ene* (**74**) *and its* 15β-*Epimer* (**75**).—A solution of the enones (**69**) and (**70**) (2.0 g, 5.5 mmol) and sodium cyanoborohydride (416 mg, 6.6 mmol) in methanol (30 ml) was maintained at pH 4 by addition of dil. hydrochloric acid. After 30 min at room temperature, work-up with ether and purification by chromatography [silica; ether–light petroleum (3:7)] furnished an oil (1.48 g, 73%) which was subjected to h.p.l.c. Elution with light petroleum–ethyl acetate (9:1) gave 12α-ethoxycarbonyl-15α-hydroxy-11-oxo-1-norprost-13-ene (**74**), $\nu_{max.}$($CHCl_3$) 3 590 (OH), 1 750 ($CO_2Et$), and 1 730 $cm^{-1}$ (C=O); δ 5.97 (1 H, d, *J* 15 Hz, C*H*=CHCHOH), 5.65 (1 H, dd, *J* 7, *J*′ 15 Hz, CH=C*H*CHOH), and 5.81 (3 H, m, C*H*OH and $CO_2CH_2CH_3$); *m*/*z* 366 ($M^+$). Further elution gave the 15β-isomer (**75**), $\nu_{max.}$($CHCl_3$) 3 590 (OH), 1 750 ($CO_2Et$), and 1 730 $cm^{-1}$ (C=O); δ 6.01 (1 H, d, *J* 15 Hz, C*H*=CHCHOH), 5.62 (1 H, dd, *J* 7, *J*′ 15 Hz, CH=C*H*CHOH), and 5.81 (3 H, m, C*H*OH and $CO_2CH_2CH_3$); *m*/*z* 366 ($M^+$).

A solution of the 15α-hydroxy compound (**74**) (91 mg, 0.25 mmol) in acetone (5 ml) at −20 °C was treated dropwise with Jones reagent (0.09 ml), and after 20 min the mixture was

worked up with ether to give, after chromatography [silica; ether–light petroleum (1:4)], 12α-ethoxycarbonyl-11,15-dioxo-1-norprost-13-ene (**69**) (33 mg, 36%), $\nu_{max.}$($CHCl_3$) 1 755 ($CO_2Et$), 1 730 (C=O), 1 670 and 1 622 $cm^{-1}$ (C=C–C=O); δ 7.05 (1 H, d, *J* 17 Hz, C*H*=CHCO), 6.19 (1 H, d, *J* 17 Hz, CH=C*H*CO), and 4.21 (2 H, q, *J* 7 Hz, $CO_2CH_2CH_3$). Similar oxidation of the 15β-isomer (**75**) also gave the enone (**69**) (40%).

12-*Ethoxycarbonyl*-1,15-*dihydroxy*-11-*oxoprost*-13-*ene* (**76**).—A solution of 12-ethoxycarbonyl-1-hydroxy-11,15-dioxoprost-13-ene (0.2 g, 0.51 mmol) [(**71**) and (**72**), in the ratio *ca.* 8:1] in methanol (5 ml) was treated with sodium cyanoborohydride (38 mg, 0.6 mmol) in the manner described previously to give 12α-ethoxycarbonyl-1,15-dihydroxy-11-oxoprost-13-ene 12α-(**76**) (0.14 g, 70%), $\nu_{max.}$(film) 3 420 (OH), 1 735 ($CO_2Et$), and 1 715 $cm^{-1}$ (C=O); δ 6.01 and 5.97 (1 H, 2 d, *J* 17 Hz, C*H*=CHCHOH in the two 15-epimers), 5.62 and 5.61 (1 H, 2 dd, *J* 17, *J'* 7 Hz, CH=C*H*CHOH in the two 15-epimers) [additional doublets at δ 5.86 and 5.85 (each with *J* 17 Hz) indicated the presence of *ca.* 12% of the 12β-ethoxycarbonyl isomers], 4.16 (2 H, q, *J* 7 Hz, $OCH_2CH_3$), 4.1 (1 H, s, OH), 3.61 (2 H, t, *J* 7 Hz, $CH_2OH$), 2.65 (2 H, m, $CH_2CH_2CO$), and 0.88 (3 H, m, $CH_2CH_3$); *m/z* 396 ($M^+$).

*Methyl* 12-*Ethoxycarbonyl*-11,15-*dioxoprost*-13-*enoate* (**73**).—A solution of 12-ethoxycarbonyl-1-hydroxy-11,15-dioxoprost-13-ene [(**71**) and (**72**), in the ratio *ca.* 8:1] (310 mg, 0.76 mmol) in dimethylformamide (58 ml) was treated with pyridinium dichromate (1.26 g, 3.9 mmol) and stirred at room temperature overnight. The mixture was poured into water, and worked up with ether to give an oil which was purified by chromatography (silica; ether) before being dissolved in ether (10 ml) and treated with a solution of diazomethane (0.79 mmol) in ether for 15 min at 0 °C. Evaporation of the solvent, and chromatography of the residue (silica; ether), gave the *product* (**73**) (containing *ca.* 12% of the 12β-isomer) (150 mg, 47%), $\nu_{max.}$(film) 1 740 ($CO_2Me$), 1 720 (C=O), 1 680 $cm^{-1}$ (C=C–C=O); δ 7.05 and 6.91 (relative intensity 8:1, 1 H, both d, *J* 17 Hz, C*H*=CHCO in 12α- and 12β-isomer respectively), 6.19 and 6.09 (relative intensity 8:1, 1 H, both d, *J* 17 Hz CH=C*H*CO in 12α- and 12β-isomer respectively), 4.22 (2 H, m, $CO_2CH_2CH_3$), 3.65 (3 H, s, $CO_2CH_3$), 2.62 (2 H, m, $CH_2CO_2Me$), 2.3 (2 H, m, CH=CHCOC$H_2$), and 0.88 (3 H, m, $CH_2CH_3$); *m/z* 422 ($M^+$) (Found: C, 68.0; H, 9.4. $C_{24}H_{38}O_6$ requires C, 68.2; H, 9.1%).

*Methyl* 12-*Ethoxycarbonyl*-15-*hydroxy*-11-*oxoprost*-13-*enoate* (**77**).—The enone (**73**) (150 mg, 0.36 mmol), dissolved in methanol (10 ml), was reduced with sodium cyanoborohydride (27 mg, 0.43 mmol) at pH 4 for 30 min at room temperature. The usual work-up with ether, followed by chromatography (silica; ether), gave the product (**77**) (60 mg, 40%) (as a mixture of isomers at C-12 and C-15), $\nu_{max.}$(film) 3 400 (OH), 1 732 ($CO_2Et$), and 1 718 $cm^{-1}$ (C=O); δ 5.95 (1 H, m, C*H*=CHCHOH), 5.63 (1 H, m, CH=C*H*CHOH), 4.22 (3 H, m, C*H*OH and $OCH_2CH_3$), 3.68 (3 H, s, $CO_2CH_3$), 2.60 (2 H, m, $CH_2CO_2Me$), and 0.89 (3 H, m, $CH_2CH_3$); *m/z* 424 ($M^+$).

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