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NOVEL MOLECULAR REARRANGEMENTS OF 4-HYDROXY-2-CYCLOPENTENONES

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Abstract—Novel rearrangements of hydroxycyclopentenone derivatives **1** and **24** to **7, 9, 11** and **31, 33, 35** are reported. The stereochemistry of the rearrangement is interpreted as the result of synchronous enolate induced [1.5]-sigmatropic rearrangement and stepwise addition–elimination process. Preparation of the various substrates and structural elucidation of new products are also described.

DURING the last decade, the 4-hydroxy-2-cyclopentenones have been one of the most popular synthetic objects for organic chemists, since they are important intermediates in the preparation of natural products such as prostaglandins and the alcohol moieties of the pyrethrum esters.[1-3] While there are many methods of preparing the title compounds, relatively few investigations of their chemical transformations can be found in the literature. As part of our general program concerning the synthetic potential of cyclopentenones, we have systematically studied their reactions with nucleophilic reagents.

Recently, in connection with the synthesis of 13-thiaprostanoids we had investigated and described novel rearrangements of 4-hydroxy-2-cyclopentenones (Scheme 1).[4] The triethylamine catalysed reaction between cyclopentenone **1a** and mercaptan **2a** afforded a mixture of thiaprostaglandin **3a**, thioether **7a** and enol thioether **9a**. Mainly, on the bases of chiroptical properties of the products, for the formations of thioethers (**7a** and **9a**) we proposed an enolate induced [1.5]-sigmatropic shift on the corresponding dehydration product (**4**), followed by [1.5]-hydrogen shift (**6a** → **9a**). Blockage of the OH function of cyclopentenone by a t-butyldimethylsilyl group prevented dehydration (**3b** → **4a**) and only thiaprostaglandin derivative (**3b**) was isolated in good yield.

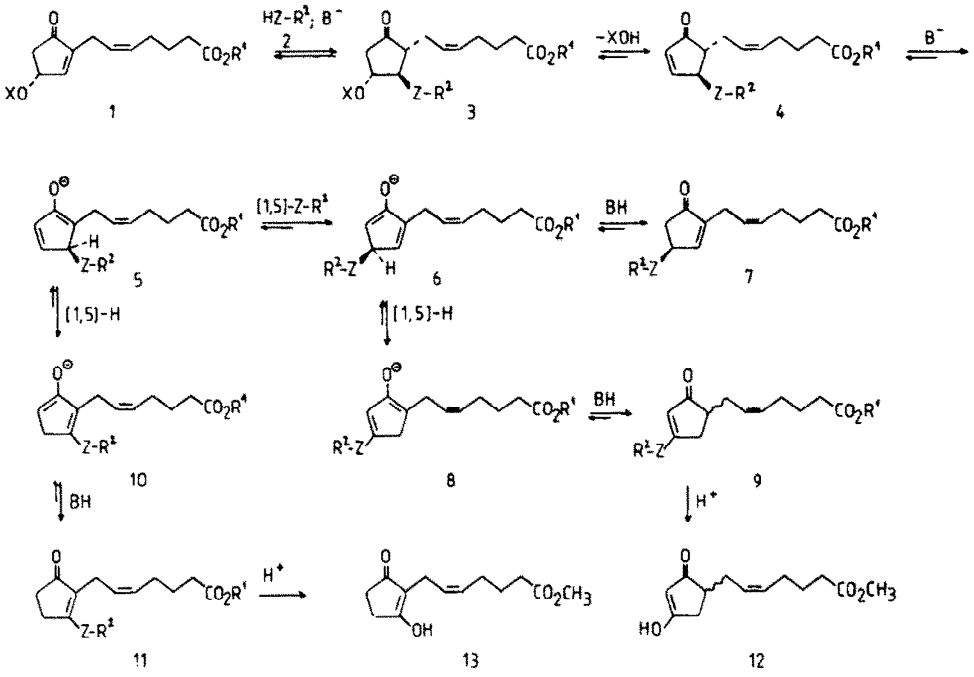
It seemed reasonable to expect that processes analogous to the above rearrangements might be induced on the hydroxycyclopentenones with alkoxide nucleophiles too. If so, that would be the first example for a concerted sigmatropic rearrangement involving an alkoxide migrating group, because to date, according to our best knowledge the migration of alkoxide group in thermal reaction has not been reported.

The reaction between hydroxycyclopentenone **1a** and sodium methoxide was carried out at 0° in methanol, using 1.0 equiv of methoxide. In contrast to the discussed reactions of S compounds, this reaction was rather fast, and gave a mixture of four products **7b**, **9b**, **11b** and a trimer in the ratio 45:5:20:30 (overall yield 77%). The structures of these new compounds were established by elemental analysis and ^{1}H-NMR spectroscopy (Experimental). Chemical support for the structural assignment was also obtained by treatment of the enol ethers **9b** and **11b** with acid; the hydrolysis afforded the corresponding cyclopentene-1,3-dione derivative (**12** and **13**, respectively).

At this stage of research we thought that a similar mechanism could be applied to explain the reaction of cyclopentenone **1a** with alkoxide as with S-nucleophiles. The first step of this proposed mechanism involves the nucleophilic 1,4-addition of methoxide anion on the enone moiety of cyclopentenone giving an unstable alkoxycyclopentanone **3b** (X = H). By analogy with the earlier cases, we expected that this addition reaction would occur preferentially on the β-side of cyclopentenone to secure the all *trans*-arrangements of the substituents. Base-catalysed dehydration of the cyclopentenone **3b** produces a cyclopentenone **4b**, which was subsequently converted into the corresponding anion **5b**. This intermediate can either undergo a [1.5]-sigmatropic methoxy shift or a [1.5]-sigmatropic H-shift to give two of the observed products (**7b** and **11b**, respectively). The third product **9b** can be formed from the intermediate anion **6b** by [1.5]-sigmatropic H-shift.

This mechanism is in fact an extension of that proposed earlier for the thiolate ion induced rearrangements of hydroxycyclopentenone. Formation of enol ether **11b** also substantiated the intermediacy of the postulated cyclopentenone **4b**.

In order to gain more information about the mechanism further examinations were undertaken. In this case, the blockage of the OH group did not prevent the rearrangement. The reaction of silyl ethers **1b** and **1c** with sodium methoxide afforded cyclopentenones **7b**, **9b** and **11b** in excellent yield. It seems likely that the first step of this reaction was also the nucleophilic addition of methoxide anion, which was followed by the elimination of silyloxy substituent (**1b** or **1c** → **4b**).



1	R	X
a	CH_3	H
b	CH_3	$Si(CH_3)_2$-t-Bu
c	CH_3	$SiBu_3$
d	CH_3	THP
e	CH_3	Ac
f	CH_3-CH_2	H
g	CH_3-CH_2	$Si(CH_3)_2$-t-Bu
h	Ph-CH_2	H
i	Ph-CH_2	$Si(CH_3)_2$-t-Bu

3-11	R^1	R^2	Z
a	CH_3	CH_2-C(HO, H)-C_5H_{11}	S
b	CH_3	CH_3	O
c	CH_3-CH_2	CH_3-CH_2	O
d	CH_3	CH_3-CH_2	O
e	CH_3-CH_2	CH_3	O

2	R^2	Z
a	CH_2-C(HO, H)-C_5H_{11}	S
b	CH_3	O
c	CH_3-CH_2	O

Scheme 1.

Previous removal of the protecting group can be ruled out, for it was found that the recovered alcohol from some incomplete reaction existed as its silyl ether (**1b** or **1c**). Since the reaction proceeded without the formation of trimer side product and the product distribution was essentially the same as in the case of unprotected cyclopentenone (**1a**), for further investigations we used the silyl ethers.

The corresponding tetrahydropyranyl ether **1d** and acetate **1e** also underwent rearrangement with methanolic sodium methoxide to give the above rearranged products (**7b**, **9b** and **11b**).

The reaction turned out to be very sensitive to the conditions. Thus, the solvent, the temperature and the time influenced the yield and the product composition considerably. Essentially, methanol was the only suitable solvent. In other primary or secondary alcohols transesterification and incorporation of the corresponding alkoxide did occur, producing a more complex mixture of products. In tertiary alcohol and in aprotic solvents (e.g. t-BuOH, THF, DMF) profound tendency of dimerization and trimerization was observed (see later).

The relative amount of these compounds **7**, **9** and **11** was a function of the temperature and of the time (Table 1). At lower temperature, after a shorter time the major product was alkoxycyclopentenone **7**, and only trace amounts of enol ethers **9** and **11** were isolated. At elevated temperature considerable amounts of the enol ether **11** was formed, especially when the temperature of

Table 1. Rearrangements of cyclopentenones under various conditions

Starting material	Base	Amount of base (equiv.)	Solvent	Temp. (±2°C)	Reaction time (hr)	Product composition (mol %) 7	9	11	Yield %
1b	CH_3ONa	1	CH_3OH	0	0.5	95	trace	5	65
1b	CH_3ONa	1	CH_3OH	20	2	64	6	30	72
1b	CH_3ONa	2	CH_3OH	20	2	65	7	28	74
1b	CH_3ONa	0.2	CH_3OH	20	2	65	6	29	62
1b	CH_3ONa	1	CH_3OH	40	2	47	10	43	68
1b	CH_3ONa	1	CH_3OH	20	48	12	58	30	65
1c	CH_3ONa	1	CH_3OH	0	1	92	2	6	78
1g	CH_3CH_2ONa	1.2	CH_3CH_2OH	0	0.5	93	2	5	68
1g	CH_3CH_2ONa	1.2	CH_3CH_2OH	20	2	62	5	33	71

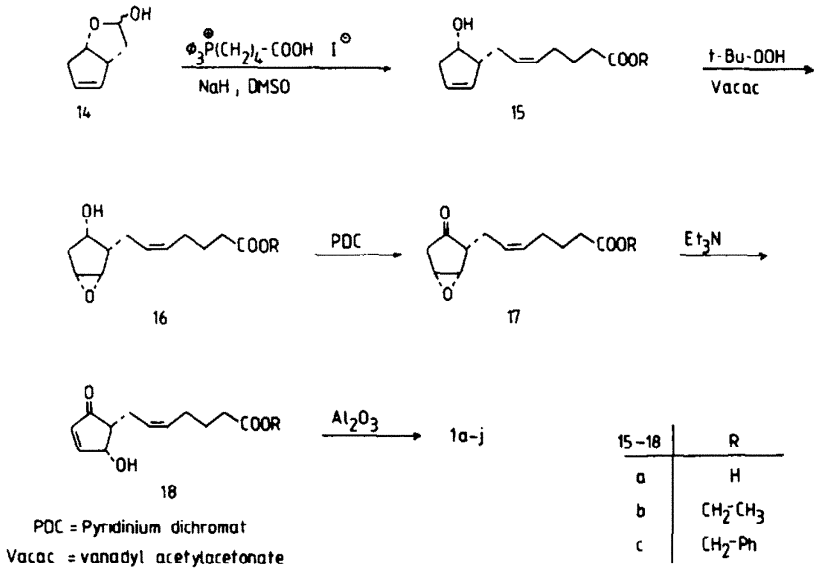
the reaction was allowed to rise to 40°. Under this condition the reaction gave **7** and **11** in approximately equal amounts. Using longer times, the amount of enol ether **9** increased and after 2 days all the alkoxycyclopentenone **7** was transformed into **9**. Furthermore, we could completely convert the isolated alkoxycyclopentenone **7** into enol ether **9** by sodium alkoxide.

The reaction was not sensitive to the amount of the catalyst. Using 0.2–2 equivalents of sodium methoxide the product composition did not change significantly. The use of lower amounts of base resulted in longer times and in incomplete transformation of the starting material.

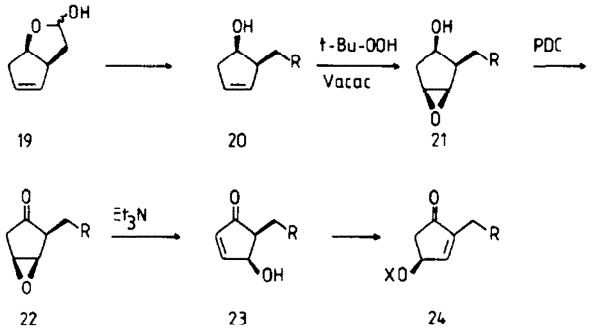
Attention was next turned to the stereochemical outcome of the rearrangement. Two of the rearrangement products, alkoxycyclopentenone **7** and enol ether **9**, have chiral centers. As was anticipated, the enol ether **9** was racemic. The [1.5]-hydrogen shift in the rearrangement of intermediate **6** had produced an achiral enolate **8**, on which the protonation was a random process.

In the formation of alkoxycyclopentenone **7**, we expected that the initial addition would occur preferentially from the less-hindered β-face and then the resultant alkoxycyclopentenone **3** broke down to cyclopentenone **4**. A concerted [1.5]-sigmatropic rearrangement with suprafacial stereochemistry on the corresponding enolate anion **5** would cause the retention of configuration, which means the inversion of the chiral center of the starting material **1** ($R \rightarrow S$). In contrast with this expectation, the isolated alkoxycyclopentenones **7** were mixtures of enantiomers (4*R* and 4*S*), e.g. in the course of the reaction racemization or/and inversion of configuration had taken place.

The above results indicated that the mechanism for the alkoxide catalysed rearrangement is more complicated than we postulated earlier. In order to gain greater insight into the stereochemical aspects of the process we planned a more detailed examination of the reactions of hydroxycyclopentenones with nucleophiles. Two series of optically active compounds were therefore synthesized, as illustrated in Schemes 2 and 3, involving the 4(*R*)-hydroxy-2-cyclopentenone deriva-



Scheme 2.



24	R	X
a	$H-C=C(-(CH_2)_3-COOCH_3)-H$	H
b	$H-C=C(-(CH_2)_3-COOCH_3)-H$	$Si(CH_3)_2$-t-Bu
c	$H-C=C(-CH_2-CH_3)-H$	H
d	$H-C=C(-CH_2-CH_3)-H$	$Si(CH_3)_2$-t-Bu
e	$H-C=C(-CH_2-CH_3)-H$	$SiBu_3$
f	$-(CH_2)_3-CH_3$	H
g	$-(CH_2)_3-CH_3$	$Si(CH_3)_2$-t-Bu
h	$-CH_2-OCPh_3$	H
i	$-CH_2-OCPh_3$	$Si(CH_3)_2$-t-Bu

20-23	R
a	$H-C=C(-(CH_2)_3-COOR')-H$
b	$H-C=C(-CH_2-CH_3)-H$
c	$-(CH_2)_3-CH_3$
d	$-CH_2-OCPh_3$

Scheme 3.

tives (**1**) and derivatives having 4(*S*)-configuration (**24**).

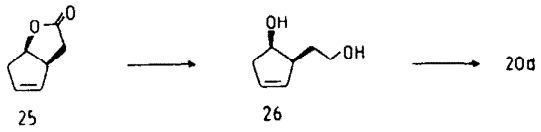
For the syntheses of these compounds as well as the corresponding protected analogues we used essentially the same procedure that was published earlier for the preparations of prostaglandin-E_2 synthon (**1a**).[9] Thus, the 4(*R*)-hydroxycyclopentenones (**1a–i**) were prepared from the optically active olefin-lactol **14**. Condensation of the lactol with the ylide generated from 4-carboxybutyltriphenylphosphonium iodide provided the cyclopentenol **15a**, which was converted to the corresponding ester (**15b, c**) by esterification with the appropriate alcohol. Epoxidation of **15** with t-butyl hydroperoxide and vanadyl acetylacetonate yielded the epoxyalcohol **16**, which was oxidized to the epoxy ketone **17** utilizing pyridinium dichromate in DMF. Treatment of the latter with triethylamine, followed by rearrangement of the resultant cyclopentenone **18** on alumina, afforded optically pure 4(*R*)-hydroxycyclopentenone derivative **1**.

In a similar way, starting from the enantiomeric lactol **19** we obtained the 4(*S*)-hydroxycyclopentenone **24a** (Scheme 3). In analogous fashion, the pyrethroid alcohol **24c** was also synthesized from the lactol **19**. Condensation of this lactol with the Wittig reagent derived from propyltriphenylphosphonium bromide and dimsyl sodium provided the cyclopentenol **20b**, which was oxidized with t-butyl hydroperoxide and vanadyl acetylacetonate. The resulting epoxyalcohol **21b** was oxidized with pyridinium dichromate and the epoxyketone **22b** so produced was treated with triethylamine. The rearrangement of the product **23b** yielded hydroxycyclopentenone **24c**.

Intermediate **20b** was used for the preparation of **24f**, which incorporated a saturated side chain. Catalytic reduction of **20b** over Pd catalyst, followed by sequential oxidation of the resulting cyclopentenone **20c** with t-butyl hydroperoxide and pyridinium dichromate gave the epoxyketone **22c**. Treatment of the latter with ethereal triethylamine afforded the cyclopentenone **23c**, which was converted into the desired hydroxycyclopentenone **24f** by rearrangement on alumina.

The trityloxy derivatives **24h** were prepared from the optically active lactone **25** (Scheme 4). Reduction of this lactone with $LiAlH_4$ afforded cyclopentenol **26**, which was tritylated and the resulting trityl ether **20d** was converted onto the desired hydroxycyclopentenone **24h** with the above procedures via intermediates **21d**, **22d** and **23d**.

The rearrangement of hydroxycyclopentenone **24** was carried out under a variety of reaction conditions (Table 2), in each case by the addition of the hydroxycyclopentenone to an alcoholic solution of the base at the appropriate temperature. The structures of the products (**31**, **33** and **35**, Scheme 5) were assigned from their spectral data. The enantiomeric composition of the product **7** and **31** was established by comparing their optical rotation with that of the corresponding hydroxycyclopentenone (**1** and **24**: X = H, respectively). Since no chiroptical data of 4-



25 26

Scheme 4.

alkoxycyclopentenones were available, there was no direct way to assess the stereospecificity of the rearrangement.[10,11] Thus, we had to rely on the careful comparison of the trend of the sign and magnitude of the optical rotation of hydroxycyclopentenone and their O-protected derivatives. The optical rotations of the hydroxycyclopentenones and their derivatives were close to each other and of the same sign. The OMe group is rather similar in size to the OH group and therefore we have assumed that the optically pure 4-alkoxycyclopentenone would have the same sign and magnitude of rotation as its OH-analogues, and so we used the optical rotation value of hydroxycyclopentenones in our calculations. Although this assumption is not strictly correct, the error introduced by it is rather minor.

As expected, almost identical product composition (**31a**, **33a** and **35a**) and an inverse enantiomeric ratio was obtained in the rearrangement of **24b** as from the reaction of prostaglandin synthon (Table 2).

The reaction of the pyrethroid alcohol **24c** with alkoxide gave the alkoxycyclopentenone **31b** in excellent yield. In this case, the enol ethers **33b** and **35b** were formed in only trace amounts. Noteworthy was the fact that the stereochemistry of the process (**24d** → **31b**) was highly dependent upon the temperature. At lower temperature (−20°) we got partial inversion of configuration and retention of configuration predominated at ambient temperature.

A similar ratio of isomers (**31d**, **33d** and **35d**) had been obtained in the rearrangement of the saturated analogue **24g**. Furthermore, an exclusive formation of alkoxycyclopentenone **31d** was achieved at lower temperature. The process (**24g** → **31d**) proceeded with high inversion of configuration at C-4.

By contrast, the trityl ether **24i** having the bulky side chain gave essentially the same product composition and enantiomeric ratio of the alkoxycyclopentenone product **31e**, as we have observed in the cases of prostaglandin synthons. All attempts to isolate the benzyloxy migration product as a result of the reaction of ester **1i** with sodium benzylate in benzyl alcohol failed.

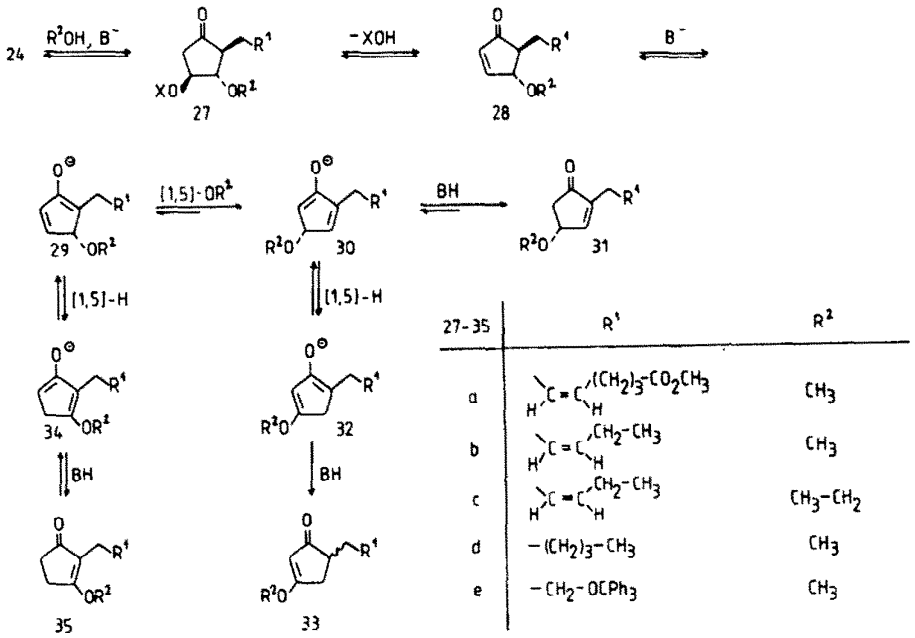
Likewise, no trace of migration product was observed when hydroxycyclopentenone (**1** or **24**) was exposed to lithium diisopropylamide or potassium t-butoxide. From the reaction of hydroxycyclopentenone **1b** with one equivalent of lithium diisopropylamide we isolated in a moderate yield (31%) the dimer **37b**, identified by the usual techniques (Experimental). Probably, this highly basic and poorly nucleophilic reagent partially converted the substrate into the corresponding enolate anion **36b**, which then initiated a nucleophilic 1,4-addition across the enone system of **1b**. An identical result was obtained from the reaction of **24g** with lithium diisopropylamide, leading to dimer **42c** in 42.5% yield.

A more complicated picture emerged from the reaction of hydroxycyclopentenone **1b** with potassium t-butoxide in t-butanol. Here, a complex mixture of

Table 2. Selectivity of the base catalysed rearrangements of hydroxycyclopentenone derivatives (**1** and **24**) at various reaction temperatures†

Substrate	Configuration of the substrate	Base (Solvent)	Product‡	Enantiomeric composition (%),§ Reaction temperature (°C)		Configuration of major enantiomer, (Reaction time, hr)	
				−20 (12)	0 (3)	20 (1)	40 (1)
1b	*R*	MeONa (MeOH)	**7b**	—	74–26, *R*	80–20, *R*	82–18, *R*
1c	*R*	MeONa (MeOH)	**7b**	—	—	78–22, *R*	—
24b	*S*	MeONa (MeOH)	**31a**	—	72–28, *S*	75–25, *S*	—
1g	*R*	EtONa (EtOH)	**7c**	—	—	80–20, *R*	—
24d	*S*	MeONa (MeOH)	**31b**	65–35, *R*	52–48, *S*	66–34, *S*	73–27, *S*
24d	*S*	EtONa (EtOH)	**31c**	—	—	64–36, *S*	70–30, *S*
24g	*S*	MeONa (MeOH)	**31d**	76–24, *R*	70–30, *R*	64–36, *R*	—
24i	*S*	MeONa (MeOH)	**31e**	—	68–32, *S*	53–47, *S*	—

† The reactions were carried out with a molar ratio of substrate–base–solvent of 1 : 1 : 15, at the appropriate temperature.
‡ A mixture of *R*- and *S*-isomers.
§ Average of two or more runs. Estimation errors of ± 10%.

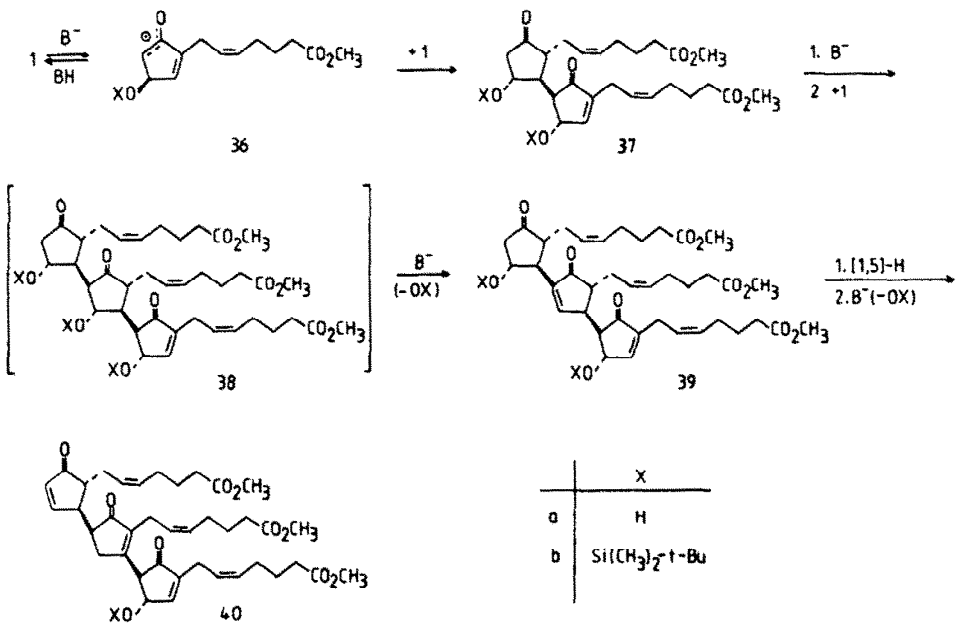


Scheme 5.

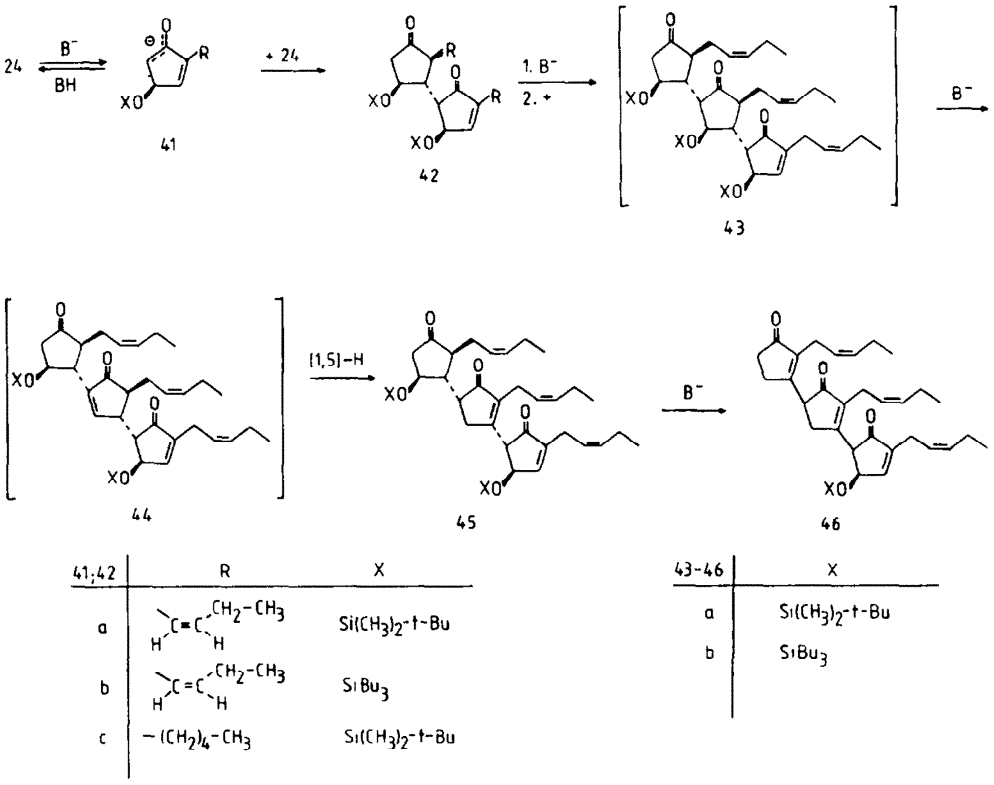
products had been formed and only the major constituent was isolated. The structure of this compound showed great resemblance to that of trimer isolated earlier from the reaction of hydroxycyclopentenone **1a** with methoxide. Therefore, we turn back to the structure elucidation of this compound.

The mass spectrum of this compound with a molecular ion M^+ 687 ($C_{39}H_{50}O_{10}$) showed that it was a trimer of the starting hydroxycyclopentenone (**40a**) formed with the loss of two water molecules (Scheme 6). The IR absorptions were indicative of three enone systems (1715, 1710 and 1700 cm^{-1}) and an OH group (3420 cm^{-1}). The ^{1}H-NMR spectrum revealed that two of the three olefinic protons of the three molecules of the starting material had been replaced by two new olefinic protons. These appeared as two one-proton multiplets at δ 5.94 and 7.35, which were very characteristic of the vicinal protons of 2-cyclopentenones. The spectrum included a signal at δ 4.25 attributable to a methine attached to oxygen and a signal at δ 5.35 indicating the presence of six olefinic protons in the side chains of the molecule. There was also a signal at δ 7.2 suggesting the presence of a β-hydrogen on one of the enone systems of the molecule.

It is likely that the first stage of the trimerization is the formation of the dimer **37a** which could not be isolated;



Scheme 6.



41,42	R	X
a	$-C(H)=C(H)-CH_2-CH_3$	$Si(CH_3)_2$-t-Bu
b	$-C(H)=C(H)-CH_2-CH_3$	$SiBu_3$
c	$-(CH_2)_4-CH_3$	$Si(CH_3)_2$-t-Bu

43-46	X
a	$Si(CH_3)_2$-t-Bu
b	$SiBu_3$

Scheme 7.

subsequently a 1,4-addition reaction of this dimer with the enolate anion **36a** gives the intermediate **38a** which may undergo base-catalysed dehydration to produce **39a**. Base-catalysed enolization on the β-ring of the trimer **39a** followed by [1.5]-hydrogen shift, and elimination of water give rise to **40a**.

The product of the reaction of **1b** with t-butoxide was the silyloxy derivative of the above trimer (**40a**). For the formation of this compound (**40b**) we suggest a similar sequence of reactions (Scheme 6).

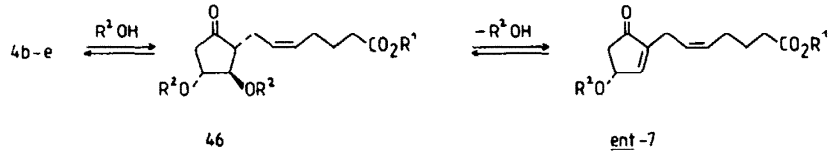
Similar results were obtained starting from substrates **24d** and **24e**. Here, in addition to the major product **45** observed previously, roughly an equal proportion of another trimer **46** was obtained and identified through its spectroscopic properties. The proposed pathways for the formation of these compounds are shown in Scheme 7.

The formation of the trimers can be explained by the nature of t-butoxide base. By comparison with methoxide or ethoxide, t-butoxide anion is slightly more basic and less nucleophilic. Consequently, the addition of the bulky t-butoxide to hydroxycyclopentenone must be necessarily slower than that observed with methoxide, and may not compete with the dimerization or trimerization processes.

It is more difficult to explain the stereochemistry of the formation of the alkoxycyclopentenone **7** and **31**. At first glance, our result seems to contradict the proposed mechanism, since the stereochemistry of the rearrangement depended strongly upon the temperature. The most plausible explanation is that a totally synchronous mechanism, as indicated in Schemes 8 and 9, in which the addition of further alkoxide anion on the intermediate **4** or **28** and then the elimination of the first OR^2 group from intermediate **46** or **47** takes place, is also operative. This stepwise ionic reaction proceeds with the retention of the configuration of the chiral center (C-4).

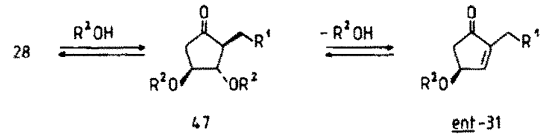
In the cases of pyrethroid alcohols **24d, e** and **24g**, the inversion of configuration was observed at lower temperature, indicating that along with the concerted [1.5]-sigmatropic shift the addition–elimination mechanism had been operating only to a slight extent. Here, the decreased formation of enol ethers **35b–d** also suggest a fast alkoxy migration on the cyclopentenone intermediates **28b–d**.

On the other hand, with the prostaglandin synthons **1b, c** and **24b** and trityl ether **24i**, we got mainly retention of configuration showing the significant involvement of the addition–elimination pathway. This



46 ent-7

Scheme 8.



Scheme 9.

mechanism is dominant in the rearrangement of both groups of substrates at higher temperature.

Finally, the reaction of the 5-substituted hydroxycyclopentenone **18** and **23**, or their silyloxy derivatives with alkoxide gave also the rearrangement products (**7**, **9**, **11** and **31**, **33**, **35** respectively). The mechanism of these reactions is probably similar to those described above. For instance, nucleophilic addition of methoxide on the enone moiety of **18** give rise to hydroxycyclopentenone **27** ($R^2 = H, X = CH_3$) which then undergoes dehydration to produce alkoxycyclopentenone **7b**. Further addition reaction of methoxide anion with the latter yields dialkoxycyclopentanone **27a** ($X = CH_3$), which may produce the key intermediate (**28a**) of the discussed rearrangement by the elimination of methanol. Another competitive reaction may be the base-catalysed isomerization of **18** into **1**.

The question may arise that if the initial 1,4-addition of alkoxide anion on the enone moiety of cyclopentenone did not occur exclusively *trans* to the groups at C-2 and C-4, then the rearrangement of the *all-cis* side product (C-3 epimers of **3**) would lead to the opposite enantiomers of **7**. Thus the *R*:*S* ratios would partly reflect the stereochemistry of the 1,4-addition reaction. We are also inclined to favour the *trans*-addition pathway in this case, for all of the conjugate addition reactions of 2,4-disubstituted-2-cyclopentenones so far described exclusively led to *trans*-*trans*-trisubstituted-cyclopentanones. However, the alternate mechanism cannot be entirely excluded because we have no direct evidence for the stereochemistry of intermediate **3**.

In summary, all the experimental observations indicated above appear to be consistent with these two alternative mechanisms. The factors determining the ratio of their involvement in the rearrangement of hydroxycyclopentenone and the observed different behaviour of the prostaglandin synthons and pyrethroid alcohols are presently under investigation.

EXPERIMENTAL

IR spectra were obtained with a Spectromom 2000 Spectrometer. NMR spectra measurements were carried out using a JEOL-FX-100 NMR Spectrometer. All signals are expressed as δ-values ppm downfield from TMS used as an internal standard. Following abbreviations are used: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), broad (br).

MS measurements were taken on a JEOL O1SG-2 double focusing mass spectrometer of Mattauch–Herzog geometry equipped with an EI ion source. The structure of the main fragments of the spectra were justified by measuring the metastable ions. Metastable peaks were determined from fragmentations in the 1st FFR, i.e. the region between the source slit and the electric sector. All signals were recorded by scanning the accelerating voltage. An initial accelerating voltage of 5 kV was used. Samples were introduced into the mass spectrometer by a direct inlet probe. The following ion source conditions were used: electron energy 75 eV, electron current 200 μA, ion accelerating voltage 10 kV.

HPLC chromatographic analyses were performed on a Du Pont 830 instrument equipped with UV detector. Stationary phase: straight phase Chromsil 10 μm (silica gel; 25 cm × 4.6 mm) or reverse phase Chromsil C-18 10 μm (25 cm × 4.6 mm), eluents CH_2Cl_2, n-hexane, MeOH–H_2O 4:1, respectively. Optical activity was determined on a Schmidt–Haensch polarimeter.

The silica gel used was obtained from Merck and that used for thin layer chromatography was the grade PF_{254}, whilst that used for column chromatography was Kieselgel 60. All solvents were dried over activated molecular sieves, and most reactions were carried out under argon.

(−)-Ethyl [7-(5-α-hydroxy-2-cyclopenten-α-yl)]-5(Z)-heptenoate (**15b**)

A mixture of **15a** (15.0 g, 0.07 mol),[4] EtOH (6.6 g, 0.14 mol) and 0.5 g of *p*-toluenesulfonic acid hydrate in 300 ml of benzene was heated for 8 hr in a Dean–Stark apparatus. After cooling, anhyd K_2CO_3 was added and the resulting mixture was filtered. Evaporation of the solvent afforded an oil, which was chromatographed with hexane–EtOAc (4:1) to give 14.0 g (82%) of **15b** as an oil. TLC ($CHCl_3$–acetone 7:3) $R_f = 0.72$. $[\alpha]_D^{25} -47.8°$ ($c = 2.24$, MeOH). IR (film): 3400 (OH), 1740 (C=O), 1460, 1380, 1300, 1240, 1140, 1080, 1030 cm^{-1}. ^{1}H-NMR (CCl_4): δ 1.25 (3H, t, J = 7 Hz, CH_3), 1.75 (2H, mc, CH_2, C_3), 1.9–2.75 (9H, m, $4CH_2$, CH, C_2, C_4, C_7, $C_{4'}$, $C_{1'}$), 4.14 (2H, q, J = 7 Hz, CH_2—O), 4.4 (1H, mc, CH—O), 5.5 (2H, mc, CH=CH, C_{5-6}), 5.68 (2H, mc, brs, CH=CH, $C_{2'-3'}$). MS: M^+ 238 (7), *m/e* 220 (32), 192 (15), 174 (17), 164 (7), 155 (23), 154 (22), 146 (13), 136 (5), 132 (45), 127 (13), 119 (27), 109 (69), 105 (22), 91 (50), 88 (23), 83 (62), 81 (100), 67 (76), 55 (70), 43 (77), 41 (53).

(−)-Ethyl [7-(5-α-hydroxy-2,3-α-epoxycyclopent-α-yl)]-5(Z)-heptenoate (**16b**)

To a stirred soln of **15b** (15.6 g, 0.066 mol) and 0.2 g of vanadyl acetylacetonate in dry benzene (150 ml) was added dropwise t-butyl hydroperoxide (14.85 g, 0.165 mol) and the resulting soln was refluxed for 4 hr. After cooling, the mixture was filtered from the ppt, the solvent evaporated and the residue was chromatographed with benzene–EtOAc (7:3) to give 10.3 g (62%) of **16b** as an oil. TLC (benzene–EtOAc 3:2) $R_f = 0.64$. $[\alpha]_D^{25} -13.2°$ ($c = 1.06$, MeOH).

IR (film): 3450 (OH), 1730 (C=O), 1450, 1420, 1380, 1310, 1230, 1170, 1145, 1100, 1070, 1035 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.22 (3H, t, J = 7 Hz, CH_3), 1.75 (2H, mc, CH_2, C_3), 1.9–2.55 (9H, m, $4CH_2$, CH, C_2, C_4, C_7, $C_{4'}$, $C_{1'}$), 3.55 (2H, dd, J = 4 Hz and 1.5 Hz, 2CH—O, $C_{2'-3'}$), 3.9 (1H, m, CH—O, C_3), 4.08 (2H, q, J = 6 Hz, CH_2—O), 5.48 (2H, mc, CH=CH). MS: M^+ 254 (2), *m/e* 236 (8), 209 (14), 191 (9), 182 (6), 154 (66), 145 (31), 135 (31), 125 (33), 109 (40), 82 (70), 81 (100), 67 (53), 55 (36).

(−)-Ethyl [7-(2,3-α-epoxy-5-oxo-cyclopent-α-yl)]-5(Z)-heptenoate (**17b**)

To a stirred soln of pyridinium dichromate (77.5 g, 0.206 mol) in dry DMF (160 ml) was added a soln of **16b** (12.5 g, 0.052 mol) in dry DMF (30 ml) and the resulting mixture was stirred for 3 hr at room temp. The mixture was poured into water (1:1) and extracted with ether (5 × 200 ml). The ethereal extract was washed with brine, dried and the solvent removed under reduced pressure to give **17b** (11.9 g, 96%) as a yellowish oil. TLC (benzene–EtOAc 3:2) $R_f = 0.82$. $[\alpha]_D^{20} -58°$ ($c = 1$, MeOH).

IR film: 1750, 1740 (C=O), 1460, 1380, 1320, 1240, 1200, 1180, 1160, 1100, 1040 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.12 (3H, t, J = 7 Hz, CH_3), 1.87 (2H, mc, CH_2, C_3), 1.9–2.7 (9H, m, 4CH_2, CH, C_2, C_4, C_7, $C_{4'}$, $C_{1'}$), 3.7 (2H, br s, 2CH—O), 4.08 (2H, q, J = 7 Hz, CH_2—O), 5.48 (2H, mc, CH=CH). MS: M^+ 252 (3), *m/e* 207 (5), 189 (6), 154 (37), 109 (27), 98 (11), 81 (45), 79 (80), 73 (100), 67 (20).

R,R-(−)-*Ethyl* 7-(5-*hydroxy*-2-*oxo*-3-*cyclopenten*-1-*yl*)-5(Z)-*heptenoate* (**18b**)

To a stirred soln of **17b** (6.7 g, 0.03 mol) in 1:1 Et_2O—CH_2Cl_2 (60 ml) was added Et_3N (6 g, 0.026 mol) and the mixture was allowed to stand overnight. Removal of the solvent *in vacuo* afforded 5.5 g (82%) of crude **18b** as an oil. TLC (benzene–EtOAc 3:2) R_f = 0.46. $[\alpha]_D^{25}$ −40° (*c* = 1, MeOH). IR (film): 3350 (OH), 1730, 1710 (C=O), 1655 (C=C), 1460, 1385, 1340, 1315, 1245, 1165, 1110, 1045 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.23 (3H, t, J = 7 Hz, CH_3), 1.72 (2H, mc, CH_2, C_3), 1.9–2.7 (7H, m, 3CH_2, CH, C_2, C_4, C_7, $C_{1'}$), 3.25 (1H, m, exchanged by D_2O, OH), 4.08 (2H, q, J = 7 Hz, CH_2—O), 4.98 (1H, mc, CH—O), 5.44 (2H, mc, CH=CH), 6.17 (1H, dd, J = 6 Hz and 1.5 Hz, CH=C, $C_{3'}$), 7.56 (1H, dd, J = 6 Hz and 1.5 Hz, C=CH, $C_{4'}$). MS: M^+ 252 (6), *m/e* 234 (47), 207 (28), 189 (21), 188 (25), 160 (29), 154 (23), 146 (31), 133 (20), 123 (30), 109 (54), 98 (100), 81 (96), 80 (44), 79 (58), 67 (53), 55 (63).

R-(+)-*Ethyl* 7-(3-*hydroxy*-5-*oxo*-1-*cyclopentenyl*)-5(Z)-*heptenoate* (**1f**)

To a stirred soln of **18b** (5.3 g, 0.02 mol) in Et_2O (50 ml) was added water (2.25 ml) and alumina (50 g; Brockmann grade II, neutral) and the resulting mixture was left to stand at room temp for 48 hr. The mixture was transferred onto a short column and then eluted with CH_2Cl_2. The soln was dried and the solvent removed under reduced pressure to give 2.4 g (45%) of **1f** as a yellowish oil. TLC (benzene–EtOAc 3:2) R_f = 0.42. $[\alpha]_D^{25}$ +11° (*c* = 1, MeOH).

IR (film): 3350 (OH), 1740, 1715 (C=O), 1630 (C=C), 1460, 1430, 1385, 1320, 1190, 1150, 1100, 1035 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.22 (3H, t, J = 7 Hz, CH_3), 1.65 (2H, mc, CH_2, C_3), 1.9–2.65 (6H, m, 3CH_2, C_2, C_4, $C_{4'}$), 2.88 (2H, mc, CH_2, C_7), 4.07 (2H, q, J = 7 Hz, CH_2—O), 4.88 (1H, mc, CH—O), 5.48 (2H, mc, CH=CH), 7.16 (1H, mc, C=CH). MS: M^+ 252 (< 1), *m/e* 234 (10), 207 (4), 189 (8), 160 (26), 146 (19), 133 (15), 132 (13), 119 (23), 117 (13), 107 (17), 105 (14), 91 (41), 81 (23), 79 (41), 77 (36), 67 (44), 55 (38), 53 (32), 43 (80), 41 (88), 39 (63), 29 (100).

t-Butyldimethylsilyl ether derivative (**1g**). This material was prepared in 89% yield by standard procedure. TLC (hexane–EtOAc 7:3). R_f = 0.57. $[\alpha]_D^{25}$ +15° (*c* = 1, MeOH).

IR (film): 1735, 1710 (C=O), 1630 (C=C), 1460, 1345, 1280, 1240, 1170, 1140, 1080, 1030, 1000, 960, 890, 830, 770 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 0.12 [6H, s, $Si(CH_3)_2$], 0.9 [9H, s, $C(CH_3)_3$], 1.24 (3H, t, J = 7 Hz, CH_3), 1.72 (2H, mc, CH_2, C_3), 1.9–2.7 (6H, mc, 3CH_2, C_2, C_4, $C_{4'}$), 1.9 (2H, mc, CH_2, C_7), 4.1 (2H, q, J = 7 Hz, CH_2—O), 4.86 (1H, mc, CH—O), 5.48 (2H, mc, CH=CH), 7.04 (1H, mc, C=CH). MS: M^- 366 (2), *m/e* 321 (11), 309 (88), 263 (19), 234 (13), 189 (47), 171 (11), 147 (8), 143 (13), 129 (13), 119 (18), 91 (23), 79 (12), 75 (100), 73 (54), 55 (15).

(−)-*Benzyl* [7-(5α-*hydroxy*-2-*cyclopenten*-α-*yl*)]-5(Z)-*heptenoate* (**15c**)

This compound was prepared, in 54% yield, as described for **15b** from the reaction of **15a** and benzyl alcohol. The oily product had R_f = 0.77 ($CHCl_3$–acetone 7:3). $[\alpha]_D^{25}$ −31 (*c* = 1.07, MeOH).

IR (film): 3350 (OH), 1735 (C=O), 1500, 1460, 1380, 1360, 1300, 1230, 1140, 1070, 1040, 1020 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.5–2.8 (11H, m, 5CH_2, CH, C_{2-4}, C_7, $C_{1'}$, $C_{4'}$), 4.5 (1H, mc, CH—O), 5.1 (2H, s, CH_2—O), 5.4 (2H, mc, CH=CH, C_{5-6}), 5.7 (2H, br s, CH=CH, $C_{2'-3'}$), 7.45 (5H, br s, aromatic protons). MS: M^+ 300 (2), *m/e* 282 (5), 256 (6), 209 (11), 191 (50), 173 (15), 145 (13), 131 (36), 129 (12), 127 (12), 119 (6), 117 (11), 108 (25), 107 (26), 91 (100), 83 (50), 79 (51), 77 (35), 67 (28), 65 (22), 55 (35).

(−)-*Benzyl* [7-(5α-*hydroxy*-2,3-α-*epoxycyclopent*-α-*yl*)]-5(Z)-*heptenoate* (**16c**)

This compound was prepared from **15c** (15.6 g, 0.052 mol) and t-butyl hydroperoxide (14.85 g, 0.165 mol) using the above method. The oily product (9.65 g, 59%) had R_f = 0.62 (benzene–EtOAc 3:2). $[\alpha]_D^{25}$ −10.8° (*c* = 0.96, MeOH).

IR (film): 3450 (OH), 1725 (C=O), 1500, 1460, 1440, 1420, 1320, 1240, 1180, 1150, 1110, 1070, 1050 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.8 (2H, mc, CH_2, C_3), 1.9–2.55 (9H, m, 4CH_2, CH, C_2, C_4, C_7, $C_{4'}$, $C_{1'}$), 3.58 (2H, dm, J = 3 Hz, 2CH—O, $C_{2'-3'}$), 3.9 (1H, mc, CH—O, $C_{5'}$), 4.7 (1H, m, OH), 5.12 (2H, s, CH_2—O), 5.62 (2H, mc, CH=CH), 7.48 (5H, br s, aromatic protons). MS: M^+ 316 (< 1), *m/e* 225 (2), 207 (14), 161 (8), 147 (7), 143 (7), 133 (6), 129 (11), 119 (13), 108 (23), 107 (28), 91 (100), 79 (85), 77 (61), 65 (73).

(−)-*Benzyl* [7-(2,3-α-*epoxy*-5-*oxo*-*cyclopent*-α-*yl*)]-5(Z)-*heptenoate* (**17c**)

This compound was similarly prepared, in 75% yield, from the reaction of **16c** and pyridinium dichromate, as described for **17b**. It had R_f = 0.85 (benzene–EtOAc 3:2). $[\alpha]_D^{25}$ −45.6° (*c* = 1, MeOH).

IR (film): 1750, 1730 (C=O), 1500, 1460, 1330, 1300, 1245, 1200, 1140, 1085, 1020 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.7 (2H, mc, CH_2, C_3), 1.9–2.7 (9H, m, 4CH_2, CH, C_2, C_4, C_7, $C_{4'}$, $C_{1'}$), 3.75 (2H, br s, 2CH—O), 5.2 (2H, s, CH_2—O), 5.52 (2H, mc, CH=CH), 7.4 (5H, s, aromatic protons). MS: M^+ 314 (3), *m/e* 236 (10), 223 (63), 216 (11), 205 (39), 187 (22), 177 (29), 167 (12), 163 (28), 159 (51), 149 (31), 145 (31), 143 (11), 135 (26), 133 (14), 131 (19), 121 (61), 117 (44), 107 (55), 105 (52), 91 (100), 79 (91), 77 (65), 67 (44), 65 (53), 55 (61).

R,R-(−)-*Benzyl* 7-(5-*hydroxy*-2-*oxo*-3-*cyclopenten*-1-*yl*)-5(Z)-*heptenoate* (**18c**)

This compound was similarly prepared, in 96% yield, from the reaction of **17c** and Et_3N, as described for **17b**; it had R_f = 0.54 (benzene–EtOAc 3:2). $[\alpha]_D^{25}$ −39.8° (*c* = 1, MeOH).

IR (film): 3300 (OH), 1730, 1705 (C=O), 1650 (C=C), 1580, 1500, 1460, 1390, 1340, 1310, 1230, 1140, 1110, 1050 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.75 (2H, m, CH_2, C_3), 1.9–2.55 (7H, m, 3CH_2, CH, C_2, C_4, C_7, $C_{1'}$), 2.88 (2H, d, J = 4 Hz, CH_2, C_7), 3.25 (1H, br s, exchanged by D_2O, OH), 5.02 (2H, s, CH_2—O), 5.42 (2H, mc, CH=CH), 6.17 (1H, dd, J = 6 Hz and 2 Hz, CH=C, $C_{3'}$), 7.3 (5H, s, aromatic protons), 7.52 (1H, dd, J = 6 Hz and 2 Hz, C=CH, $C_{4'}$). MS: M^+ 314 (3), *m/e* 236 (21), 223 (36), 205 (60), 187 (50), 177 (15), 163 (8), 159 (50), 145 (46), 135 (6), 133 (11), 131 (20), 123 (24), 122 (25), 117 (33), 107 (46), 105 (69), 98 (25), 91 (100), 86 (42), 79 (53), 77 (81), 73 (35), 55 (55).

R-(+)-*Benzyl* 7-(3-*hydroxy*-5-*oxo*-1-*cyclopentenyl*)-5(Z)-*heptenoate* (**1h**)

This compound was isolated, in 60% yield, as described for **1f** by the rearrangement of **18c**. TLC (benzene–EtOAc 3:2) R_f = 0.51. $[\alpha]_D^{25}$ +12.3° (*c* = 1.05, MeOH).

IR (film): 3400 (OH), 1730, 1710 (C=O), 1630 (C=C), 1500, 1460, 1425, 1390, 1350, 1250, 1140, 1030 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.7 (2H, m, CH_2, C_3), 1.9–2.6 (6H, m, 3CH_2, C_2, C_4, $C_{4'}$), 2.9 (2H, mc, CH_2, C_7), 4.8 (1H, mc, CH—O), 5.02 (2H, br s, CH_2—O), 5.47 (2H, mc, CH=CH), 7.07 (1H, mc, C=CH), 7.25 (5H, br s, aromatic protons). MS: M^+ 314 (2), *m/e* 297 (4), 236 (22), 223 (3), 205 (25), 187 (21), 177 (10), 163 (7), 159 (34), 156 (19), 145 (31), 139 (17), 135 (6), 133 (9), 131 (8), 119 (10), 117 (15), 108 (11), 107 (17), 91 (100), 79 (29), 77 (25), 55 (25).

t-Butyldimethylsilyl ether derivative (**1i**). This material was prepared in 82% yield by standard procedure. TLC (hexane–Et_2O 7:3). R_f = 0.54. $[\alpha]_D^{25}$ +14.6° (*c* = 1.2, MeOH).

IR (film): 1735, 1715 (C=O), 1630 (C=C), 1500, 1460, 1420, 1380, 1350, 1280, 1245, 1140, 1070, 1035, 1000, 960, 895, 830, 770 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 0.12 [6H, s, $Si(CH_3)_2$], 0.92 [9H, s, $C(CH_3)_3$], 1.75 (2H, mc, CH_2, C_3), 1.9–2.7 (6H, m, 3CH_2, C_2, C_4, $C_{4'}$), 2.89 (2H, m, CH_2, C_7), 4.88 (1H, mc, CH—O), 5.08 (2H, s, CH_2—O), 5.45 (2H, mc, CH=CH), 6.98 (1H, mc, C=CH), 7.26 (5H, s, aromatic protons). MS: M^+ 428

(6), *m/e* 371 (100), 353 (78), 296 (100), 279 (64), 261 (22), 132 (43), 120 (25), 106 (22), 91 (67), 75 (51).

(+)-7-(5β-Hydroxy-2-cyclopenten-β-yl)-5(Z)-heptanoic acid (**20a**, R′ = H)

This compound was prepared, according to the method reported for the racemic compound by Grieco and Reap, from (+)-*cis*-**19**,[12] yield: 62%. TLC ($CHCl_3$–acetone–AcOH 7:3:0.1). R_f = 0.72. $[\alpha]_D^{25}$ +45° (*c* = 1, MeOH).

IR (film): 3300 (OH), 1700 (CO), 1460, 1400, 1230, 1145, 1060 cm^{-1}. ^{1}H-NMR (CCl_4): δ 1.6 (2H, m, CH_2, C_3), 1.8–2.5 (9H, m, $3CH_2$, CH, C_2, C_4, C_7, $C_{4'}$, $C_{1'}$), 4.1 (1H, m, CH—O), 5.15 (2H, m, CH=CH, C_{5-6}), 5.38 (2H, s, CH=CH, $C_{3'-4'}$). MS: M^+ 210 (< 1), 192 (34), 174 (4), 166 (7), 132 (12), 127 (18), 119 (30), 109 (13), 105 (16), 91 (26), 83 (100), 81 (33), 79 (27), 66 (46), 55 (45), 43 (18), 41 (44), 39 (34).

(+)-7-(5β-Hydroxy-3,4-β-epoxy-2-cyclopenten-β-yl)-5(Z)-heptanoic acid (**21a**, R^1 = H)

To a stirred soln of **20a** (R^1 = H; 31.2 g; 0.13 mol) and vanadyl acetylacetonate (0.4 g) in dry benzene (150 ml) was added dropwise freshly prepared t-butyl hydroperoxide (30 g; 0.33 mol), and the resulting soln was refluxed for 30 min. The mixture was cooled to room temp, filtered, the solvent evaporated *in vacuo*, and then the residue was purified by filtration through a short column (silica gel; benzene–EtOAc 3:2) to afford **21a** (R^1 = H; 28.3 g; 95%) as an oil. TLC ($CHCl_3$–acetone–AcOH 7:3:0.1) R_f = 0.7. $[\alpha]_D^{25}$ +6.2° (*c* = 1, MeOH).

IR (film): 3300 (OH), 1710 (CO), 1460, 1280, 1220, 1160, 1060, 1040 cm^{-1}. ^{1}H-NMR (CCl_4): δ 1.2 (2H, t, J = 6 Hz, CH_2, C_3), 1.4–2.5 (9H, m, $4CH_2$, CH, C_2, C_4, C_7, $C_{4'}$, $C_{1'}$), 3.4 (2H, m, 2CH—O), 3.75 (1H, m, CH—O, $C_{5'}$), 5.4 (2H, m, CH=CH). MS: M^+ 226 (< 1), *m/e* 208 (2), 135 (6), 126 (9), 119 (10), 105 (14), 91 (27), 79 (50), 67 (51), 57 (24), 55 (37), 43 (45), 41 (100), 39 (76), 27 (81).

The corresponding **21a** (R^1 = CH_3) was formed with an excess of diazomethane in ether from the above acid. $[\alpha]_D^{25}$ +10.5° (*c* = 1, MeOH).

IR (film): 3400 (OH), 1725 (CO), 1460, 1420, 1360, 1310, 1240, 1180, 1150, 1100, 1060, 1035 cm^{-1}. ^{1}H-NMR (CCl_4): δ 1.2 (2H, m, CH_2, C_3), 1.6–2.5 (9H, m, $4CH_2$, CH, C_2, C_4, C_7, $C_{4'}$, $C_{1'}$), 3.4 (2H, m, 2CH—O), 3.58 (3H, s, OCH_3), 3.75 (1H, m, CH—O, $C_{5'}$), 5.4 (2H, m, CH=CH). MS: M^+ 240 (3), *m/e* 239 (10), 223 (9), 222 (6), 209 (4), 191 (8), 161 (12), 149 (13), 140 (67), 135 (32), 125 (28), 119 (24), 105 (26), 91 (35), 81 (80), 79 (62), 67 (66), 59 (60), 55 (53), 43 (78), 41 (100).

(+)-Methyl [7-(2,3-β-epoxy-5-oxo-cyclopent-β-yl)]-5(Z)-heptenoate (**22a**, R^1 = CH_3)

This compound was prepared in the same manner as **17b** from **21a** (R^1 = CH_3), yield: 96%. TLC (benzene–EtOAc 3:2) R_f = 0.58. $[\alpha]_D^{25}$ +61° (*c* = 1, MeOH).

IR (film): 1735 (CO), 1450, 1360, 1230, 1180, 1150, 1080 cm^{-1}. ^{1}H-NMR (CCl_4): δ 1.6 (2H, m, CH_2, C_3), 1.9–2.4 (7H, m, $3CH_2$, CH, C_2, C_4, C_7, $C_{1'}$), 2.42 (2H, br s, CH_2, C_4), 3.58 (5H, br s, OCH_3, 2CH—O), 5.42 (2H, m, CH=CH). MS: M^+ 238 (< 1), *m/e* 207 (3), 206 (2), 192 (3), 189 (6), 160 (5), 140 (49), 119 (10), 109 (21), 98 (33), 91 (30), 81 (86), 80 (81), 79 (60), 67 (68), 55 (46), 43 (59), 41 (100), 39 (72).

S,S-(+)-Methyl [7-(5-hydroxy-2-oxo-3-cyclopentenyl)]-5(Z)-heptenoate (**23a**, R^1 = CH_3)

This compound was prepared from **22a** (R^1 = CH_3) in the same manner as **18b** above to give a 70% yield of a yellow oil. TLC (benzene–EtOAc 3:2) R_f = 0.38. $[\alpha]_D^{25}$ +37° (*c* = 1, MeOH).

IR (film): 3350 (OH), 1710 (CO), 1460, 1360, 1235, 1150, 1050 cm^{-1}. ^{1}H-NMR (CCl_4): δ 1.7 (2H, m, CH_2, C_3), 1.9–2.5 (7H, m, $3CH_2$, CH, C_2, C_4, C_7, $C_{1'}$), 3.58 (3H, s, OCH_3), 4.8 (1H, m, CH—O), 5.35 (2H, d, J = 6 Hz, CH=CH, C_{5-6}), 6.05 (1H, dd, J = 6 Hz and 1.5 Hz, =CH, $C_{3'}$), 7.45 (1H, dd, J = 6 Hz and 2 Hz, =CH, $C_{4'}$). MS: M^+ 238 (4), 220 (26), 207 (8), 189 (11), 160 (17), 146 (22), 140 (28), 133 (23), 123 (22), 119 (16), 109 (32), 98 (100), 91 (27), 81 (54), 67 (43), 55 (42), 41 (54).

t-Butyldimethylsilyl ether derivative was prepared by standard procedure in 40% yield. ^{1}H-NMR ($CDCl_3$): δ 0.1 [6H, m, $(CH_3)_2Si$], 0.85 [9H, m, $(CH_3)_2C$], 1.3–2.5 (9H, m, $4CH_2$, CH), 3.58 (3H, s, OCH_3), 4.52 (1H, m, CH—O), 5.28 (2H, m, CH=CH, C_{5-6}), 6.02 (1H, dd, J = 6 Hz and 1.5 Hz, =CH, $C_{3'}$), 7.28 (1H, dd, J = 6 Hz and 2 Hz, =CH, $C_{4'}$). MS: M^+ 352 (< 1), *m/e* 351 (9) [M – H], 321 (8), 295 (92), 294 (58), 263 (18), 221 (5), 221 (17), 189 (35), 171 (14), 161 (10), 119 (7), 107 (20), 89 (27), 75 (100), 73 (55).

S-(−)-Methyl [7-(3-hydroxy-5-oxo-1-cyclopentenyl)-5(Z)-heptenoate (**24a**)

This compound was prepared from **23a** (R^1 = CH_3) according to the procedure described for **1f** above, yield: 57%. TLC (benzene–EtOAc 3:2) R_f = 0.35. $[\alpha]_D^{25}$ −14.6° (*c* = 1, MeOH).

IR (film): 3350 (OH), 1720 (CO), 1630 (C=C), 1460, 1360, 1240, 1160, 1040 cm^{-1}. ^{1}H-NMR (CCl_4): δ 1.7 (2H, m, CH_2, C_3), 1.9–2.6 (6H, m, $3CH_2$, C_2, C_4, $C_{5'}$), 2.8 (2H, m, CH_2, C_7), 3.58 (3H, s, OCH_3), 4.75 (1H, m, CH—O), 5.42 (2H, t, J = 6 Hz, CH=CH), 7.05 (1H, m, =CH). MS: M^+ 238 (3), *m/e* 220 (40), 207 (8), 189 (16), 188 (16), 160 (27), 146 (33), 133 (26), 119 (30), 107 (15), 105 (12), 94 (29), 79 (26), 67 (29), 44 (100).

t-Butyldimethylsilyl ether derivative (**24b**). This compound was obtained in 85% yield, by standard methods. TLC (benzene–EtOAc 3:2) R_f = 0.85. $[\alpha]_D^{25}$ −7.3° (*c* = 1, MeOH).

IR (film): 1730, 1710 (CO), 1630 (C=C), 1460, 1425, 1390, 1360, 1250, 1140, 1030 cm^{-1}. ^{1}H-NMR (CCl_4): δ 0.05 (6H, br s, $2CH_3$, Si—CH_3), 0.84 [9H, s, $C(CH_3)_3$], 1.75 (2H, m, CH_2, C_3), 1.8–2.55 (6H, m, $3CH_2$, C_2, C_4, $C_{5'}$), 2.78 (2H, m, CH_2, C_7), 3.52 (3H, s, OCH_3), 4.7 (1H, m, CH—O), 5.35 (2H, t, J = 6 Hz, CH=CH), 7.0 (1H, m, =CH). MS: M^+ 352 (< 1), *m/e* 351 (5), 321 (10), 295 (100), 245 (4), 220 (13), 211 (12), 189 (49), 161 (16), 143 (9), 129 (10), 119 (9), 107 (13), 83 (23), 75 (100), 73 (53).

(+)-2β-[2(Z)-pentenyl]-3-cyclopenten-1β-ol (**20b**)

This compound was prepared according to the method reported for the racemic compound by Grieco, from (+)-*cis*-**19**.[13] TLC ($CHCl_3$–MeOH 99:1) R_f = 0.6. HPLC (RP): R_t = 11.8 min, b.p. 48° (0.01 mmHg). $[\alpha]_D^{25}$ +115° (*c* = 1, MeOH).

IR (film): 3350 (OH), 1460, 1420, 1380, 1310, 1205, 1160, 1110, 1050 cm^{-1}. ^{1}H-NMR (CCl_4): δ 0.88 (3H, t, J = 7 Hz, CH_3), 1.75–2.6 (7H, m, $3CH_2$, CH, C_5, $C_{1'}$, $C_{4'}$, C_2), 4.2 (1H, q, J = 3 Hz, CH—O), 4.3 (2H, m, CH=CH, $C_{2'-3'}$), 5.48 (2H, br s, CH=CH, C_{3-4}). MS: M^+ 152 (< 1), *m/e* 134 (31), 119 (14), 109 (100), 105 (21), 83 (94), 81 (50), 79 (31), 66 (69), 55 (58).

(+)-3,4-β-Epoxy-2-[2(Z)-pentenyl)]-cyclopenten-1β-ol (**21b**)

To a stirred soln of **20b** (26.8 g, 0.176 mol) and 0.5 g of vanadyl acetylacetonate in dry benzene (300 ml) was added dropwise t-butyl hydroperoxide (37.8 g, 0.42 mol) and the soln was refluxed for 2 hr. After cooling, the mixture was filtered through a short column, the solvent evaporated and the residue was chromatographed with $CHCl_3$–MeOH (5:0.3) to give 17.6 g (60%) of **21b** as an oil. TLC ($CHCl_3$–MeOH 5:0.3) R_f = 0.47. HPLC (RP): R_t = 8.6 min. $[\alpha]_D^{25}$ +12.5° (*c* = 1, MeOH).

IR (film): 3300 (OH), 1440, 1410, 1370, 1180, 1100, 1080, 1060 cm^{-1}. ^{1}H-NMR (CCl_4): δ 0.96 (3H, t, J = 7 Hz, CH_3), 1.55–2.4 (7H, m, $3CH_2$, CH, C_5, $C_{1'}$, $C_{4'}$, C_2), 3.35 (2H, d, J = 6 Hz, 2CH—O), 3.85 (1H, m, CH—O, C_1), 5.48 (2H, m, CH=CH). MS: M^+ 168 (< 1), *m/e* 167 (23), 149 (14), 125 (13), 123 (16), 121 (21), 109 (68), 107 (21), 95 (56), 93 (34), 81 (62), 79 (55), 67 (54), 57 (50), 55 (60), 44 (100), 42 (98).

(+)-3,4-β-Epoxy-2-[2(Z)-pentenyl]-cyclopentanone (**22b**)

To a stirred soln of pyridinium dichromate (144 g, 0.383 mol) in dry DMF (300 ml) was added dropwise a soln of **21b** (16 g, 0.105 mol) in dry DMF (20 ml) and the mixture was stirred for 3 hr at room temp. The reaction was quenched by the addition of

water (1 l) and the mixture was extracted with ether (600 ml). The ethereal extract was washed with brine, dried, and evaporated to give **22b** (15 g, 86%) as an oil. TLC (CH_2Cl_2–MeOH 20:1) $R_f = 0.85$. HPLC (RP): $R_t = 9.2$ min. $[\alpha]_D^{25}$ +98° ($c = 1$, MeOH).

IR (film): 1740 (CO), 1450, 1380, 1295, 1250, 1130, 1030 cm^{-1}. ^{1}H-NMR (CCl_4): δ 0.96 (3H, t, J = 7 Hz, CH_3), 1.8–2.5 (7H, m, $3CH_2$, CH, C_5, $C_{1'}$, $C_{4'}$, C_2), 3.57 (2H, br s, 2CH—O), 5.4 (2H, m, CH=CH). MS: M^+ 166 (< 1), *m/e* 165 (18), 137 (5), 125 (11), 111 (18), 109 (72), 97 (31), 95 (26), 85 (31), 83 (34), 81 (46), 71 (43), 57 (100), 55 (63).

S,S-(+)-4-*Hydroxy*-5-[2(Z)-*pentenyl*]-2-*cyclopentenone* (**23b**)

To a stirred soln of **22b** (18 g, 0.108 mol) in 1:1 Et_2O–CH_2Cl_2 (150 ml) was added Et_3N (38 ml, 0.274 mol) and the resulting soln was stirred for 3 hr at room temp. Removal of the solvent *in vacuo* yielded 18.9 g (94%) of crude **23b** as an oil. TLC (CH_2Cl_2–MeOH 20:1) $R_f = 0.4$. HPLC (RP): $R_t = 3.6$ min. $[\alpha]_D^{25}$ +50° ($c = 1$, MeOH).

IR (film): 3300 (OH), 1705 (CO), 1460, 1440, 1390, 1150, 1100, 1040 cm^{-1}. ^{1}H-NMR (CCl_4): δ 0.95 (3H, t, J = 7 Hz, CH_3), 1.8–2.8 (5H, m, $2CH_2$, CH, $C_{1'}$, $C_{4'}$, C_5), 4.0 (1H, br s, OH), 4.78 (1H, m, CH—O), 5.3 (2H, m, CH=CH, $C_{2'-3'}$), 6.0 (1H, m, =CH, C_2), 7.45 (1H, m, =CH, C_3). MS: M^+ 166 (4), *m/e* 148 (14), 137 (7), 133 (15), 122 (7), 119 (26), 109 (12), 105 (25), 98 (23), 95 (18), 91 (48), 79 (34), 55 (51), 41 (74), 39 (100).

t-Butyldimethylsilyl ether derivative was prepared in 45% yield by standard procedure. IR (film): 1715 (CO), 1635 (C=C), 1460, 1380, 1360, 1250, 1080, 1040, 960, 900, 835, 775 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 0.1 [6H, m, $(CH_3)_2Si$], 0.9 [9H, br r, $(CH_3)_3C$], 0.93 (3H, t, J = 6 Hz, CH_3), 1.4–2.6 (5H, m, $2CH_2$, CH), 4.55 (1H, m, CH—O), 5.3 (2H, m, CH=CH), 6.05 (1H, m, =CH), 7.35 (1H, m, =CH). MS: M^+ 280 (7), *m/e* 265 (9), 223 (100), 193 (10), 181 (21), 131 (14), 129 (18), 75 (94), 73 (39).

Tetrahydropyranyl ether derivative was prepared in 65% yield by standard methods. $[\alpha]_D^{25}$ +62° ($c = 1$, MeOH). IR (film): 1710 (CO), 1630 (C=C), 1460, 1440, 1380, 1350, 1250, 1180, 1160, 1150, 1070, 1020, 960, 890 cm^{-1}. ^{1}H-NMR (CCl_4): δ 0.95 (3H, t, J = 7 Hz, CH_3), 1.3–2.6 (11H, m, $5CH_2$, CH), 3.6 (2H, m, CH_2—O), 4.7 (2H, m, 2CH—O), 5.45 (2H, m, CH=CH), 6.1 (1H, m, CH=), 7.45 (1H, m, =CH). MS: M^+ 250 (< 1), *m/e* 166 (1), 148 (6), 133 (2), 119 (6), 85 (100).

S-(−)-4-*Hydroxy*-2-[2(Z)-*pentenyl*]-2-*cyclopentenone* (**24c**)

To a stirred mixture of **23b** (16.5 g, 0.099 mol) in Et_2O (300 ml) and water (9 ml) was added alumina (400 g, Brockmann grade II, neutral) and the resulting mixture was left to stand at room temp for 3 days. The mixture was transferred onto a short column and then eluted with Et_2O. The soln was dried and the solvent removed under reduced pressure to afford an oily residue, which was purified by column chromatography (CH_2Cl_2–MeOH 20:1), yield: 9.3 g (56.4%). TLC (CH_2Cl_2–MeOH 20:1) $R_f = 0.35$. HPLC (RP): $R_t = 4$ min. $[\alpha]_D^{25}$ −17° ($c = 1$, MeOH).

IR (film): 3300 (OH), 1705 (CO), 1630 (C=C), 1460, 1440, 1400, 1350, 1310, 1250, 1060, 1030 cm^{-1}. ^{1}H-NMR (CCl_4): δ 0.9 (3H, t, J = 7 Hz, CH_3), 1.9–2.6 (4H, m, $2CH_2$, C_5, $C_{4'}$), 2.8 (2H, mc, CH_2, $C_{1'}$), 4.8 (1H, m, OH), 4.7 (1H, m, CH—O), 5.3 (2H, m, CH=CH), 7.0 (1H, m, =CH). MS: M^+ 166 (49), *m/e* 151 (5), 148 (14), 147 (14), 137 (78), 133 (39), 122 (22), 119 (51), 91 (69), 79 (47), 77 (36), 55 (81), 43 (100).

t-Butyldimethylsilyl derivative (**24d**). To a soln of **24c** (3.7 g, 0.022 mol) and t-butyldimethylsilyl chloride (4.8 g, 0.032 mol) in dry DMF (15 ml) was added imidazole (3.6 g, 0.05 mol) and the soln was left to stand at room temp for 24 hr. The mixture was poured into water (100 ml) and extracted with ether (3 × 150 ml). The ethereal extract was dried and concentrated. Purification of the residue by column chromatography (CH_2Cl_2) gave silylether (4.0 g, 82%), as an oil. TLC (CH_2Cl_2) $R_f = 0.8$. HPLC (SP): $R_t = 5.3$ min. $[\alpha]_D^{25}$ −19.8° ($c = 1$, MeOH).

IR (film): 1715 (CO), 1640 (C=C), 1480, 1420, 1400, 1360, 1300, 1260, 1195, 1165, 1090, 1050, 1005, 965, 905, 835, 815, 790 cm^{-1}. ^{1}H-NMR (CCl_4): δ 0.1 [6H, br s, $Si(CH_3)_2$], 0.82 [9H, s, $C(CH_3)_3$], 0.89 (3H, t, J = 7 Hz, CH_3), 1.82–2.6 (4H, m, $2CH_2$, C_5, $C_{4'}$), 2.8 (2H, m, CH_2, $C_{1'}$), 4.8 (1H, m, CH—O), 5.35 (2H, mc, CH=CH), 6.85 (1H, m, =CH). MS: M^+ 280 (9), *m/e* 265 (4), 223 (100), 193 (8), 181 (13), 179 (8), 165 (1), 131 (10), 91 (22), 75 (63), 73 (17).

Tributylsilyl derivative (**24e**). To a soln of **24c** (6.5 g, 0.04 mol) and tributylsilyl chloride (11.0 g, 0.046 mol) in dry DMF (25 ml) was added imidazole (6.4 g, 0.094 mol) and the resulting soln was left to stand at room temp for 24 hr. The mixture was poured onto water (100 ml) and extracted with ether (5 × 50 ml). The ethereal soln was washed with brine and dried. Evaporation of the solvent afforded an oil, which was chromatographed with CH_2Cl_2 to give **24e** (13.5 g, 91.6%), as a yellow oil. TLC (CH_2Cl_2) $R_f = 0.75$. $[\alpha]_D^{25}$ −16.8° ($c = 1$, MeOH).

IR (film): 1710 (CO), 1635 (C=C), 1465, 1410, 1380, 1355, 1300, 1180, 1080, 960, 880 cm^{-1}. ^{1}H-NMR (CCl_4): δ 0.45 (6H, m, $3CH_2$, Si—CH_2), 0.8 (9H, q, J = 6 Hz, $3CH_3$), 0.9 (3H, t, J = 7 Hz, CH_3, $C_{5'}$), 1.15 (12H, m, $6CH_2$), 1.8–2.5 (4H, m, $2CH_2$, C_5, $C_{4'}$), 2.8 (2H, mc, CH_2, $C_{1'}$), 4.75 (1H, m, CH—O), 5.3 (2H, m, CH=CH), 6.8 (1H, m, =CH). MS: M^+ 364 (11), *m/e* 307 (100), 251 (25), 221 (8), 195 (7), 148 (8), 55 (15).

(+)-3,4-*β-Epoxy*-2*β*-*pentylcyclopentan*-1*β*-*ol* (**21c**)

Epoxycyclopentanol **21b** (27.0 g, 0.16 mol) was mixed with 1 g of 10% Pd—C in 60 ml of MeOH, and the mixture was stirred under an H_2 atmosphere (1 atm) until the theoretical amount of H_2 (380 ml) had been absorbed. The catalyst was removed by filtration and the solvent evaporated in vacuum to give 22.5 g (83.3%) of the oily **21c**. TLC ($CHCl_3$–MeOH 5:1) $R_f = 0.45$. $[\alpha]_D^{25}$ +8.9° ($c = 1$, MeOH).

IR (film): 3400 (OH), 1460, 1440, 1410, 1380, 1170, 1100, 1070, 1040, 1010 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 0.94 (3H, t, J = 6 Hz, CH_3), 1.1–2.7 (11H, m, $5CH_2$, CH, C_5, $C_{1'-4'}$, C_2), 3.5 (2H, m, 2CH—O), 4.0 (1H, m, CH—O, C_1). MS: M^+ 170 (< 1), *m/e* 152 (2), 127 (10), 113 (9), 109 (19), 99 (77), 57 (100), 41 (51).

(+)-3,4-*β-Epoxy*-2*β*-*pentylcyclopentanone* (**22c**)

Epoxycyclopentanol **21c** (8.6 g, 0.05 mol) was oxidized with pyridinium dichromate (37.6 g, 0.1 mol), as described for **22b** to obtain **22c** in 78% yield. TLC (CH_2Cl_2–MeOH 100:1) $R_f = 0.3$. HPLC (RP): $R_t = 5.6$ min. $[\alpha]_D^{25}$ +91° ($c = 1$, MeOH).

IR (film): 1735 (CO), 1460, 1380, 1260, 1140, 1100, 1030, 1000 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 0.9 (3H, t, J = 6 Hz, CH_3), 1.38 (8H, mc, $4CH_2$, $C_{1'-4'}$), 2.2–2.7 (3H, m, CH_2, CH, C_5, C_1), 3.7 (2H, br s, 2CH—O). MS: M^+ 168 (6), *m/e* 150 (2), 139 (2), 125 (8), 112 (18), 97 (100), 83 (47), 55 (93).

S,S-(+)-4-*Hydroxy*-5-*pentyl*-2-*cyclopentenone* (**23c**)

Epoxyketone **22c** and Et_3N were allowed to react according to the method described for **22b**, to obtain **23c** in 98% yield. TLC (benzene–MeOH (10:1) $R_f = 0.35$. HPLC (RP): $R_t = 4$ min. $[\alpha]_D^{25}$ +84° ($c = 1$, MeOH).

IR (film): 3320 (OH), 1710 (CO), 1460, 1380, 1105, 1040 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 0.9 (3H, t, J = 6 Hz, CH_3), 1.35 (8H, mc, $4CH_2$, $C_{1'-4'}$), 2.3 (1H, m, CH), 4.9 (1H, m, CH—O), 6.15 (1H, m, =CH, C_2), 7.45 (1H, m, =CH, C_3). MS: M^+ 168 (13), *m/e* 150 (4), 139 (3), 126 (7), 121 (8), 111 (11), 98 (100), 80 (26), 55 (19).

S-(−)-4-*Hydroxy*-2-*pentyl*-2-*cyclopentenone* (**24f**)

Cyclopentenone **23c** was converted into the derivative **24f** as described for **24c** to obtain the product in 61% yield.[16] TLC (benzene–MeOH 10:1) $R_f = 0.3$. HPLC (RP): $R_t = 4$ min. $[\alpha]_D^{25}$ −12.8° ($c = 1$, MeOH).

IR (film): 3350 (OH), 1705 (CO), 1630, (C=C), 1460, 1440, 1380, 1320, 1250, 1200, 1160, 1110, 1040 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 0.8 (3H, t, J = 6 Hz, CH_3), 1.28 (6H, m, $3CH_2$, $C_{2'-4'}$), 2.0–2.8 (4H, m, $2CH_2$, C_5, $C_{1'}$), 4.85 (1H, m, CH—O), 7.1 (1H, m, =CH). MS: M^+ 168 (28), *m/e* 139 (19), 124 (100), 113 (16), 111 (25), 96 (18), 95 (18), 69 (29), 55 (37), 43 (62), 41 (50).

t-Butyldimethylsilyl derivative (**24g**). The silyl ether was prepared by the method described for **24d**. TLC (benzene–acetone 10:1) $R_f = 0.9$. HPLC (RP): $R_t = 17.6$ min. $[\alpha]_D^{25}$ $-15°$ ($c = 1$, MeOH).

IR (film): 1710 (CO), 1635 (C=C), 1460, 1405, 1380, 1350, 1290, 1250, 1190, 1160, 1080, 1005, 965, 910, 840 cm^{-1}. ^{1}H-NMR (CCl_4): δ 0.05 (6H, s, 2Si—CH_3), 0.9 [12H, s+t, CH_3, $C(CH_3)_3$], 1.35 (6H, m, $3CH_2$, $C_{2'-4'}$), 1.9–2.8 (4H, m, $2CH_2$, C_5, $C_{1'}$), 4.9 (1H, m, CH—O), 7.0 (1H, m, =CH). MS: M^+ 282 (6), 267 (4), 225 (74), 169 (100), 155 (11), 147 (12), 75 (70), 73 (27).

(+)-2β-*Hydroxyethyl*-3-*cyclopenten*-1β-*ol* (**26**)

(+)-*cis*-**25**[14] (24.8 g, 0.2 mol) in dry Et_2O (350 ml) was added dropwise to a stirred suspension of $LiAlH_4$ (9.5 g, 0.25 mol) in dry Et_2O (100 ml) at 20°, and the resulting mixture was refluxed for 2 hr. After the mixture had been cooled to 5°, water was added and then the ppt was collected by filtration. The solid was dissolved in dil HCl and extracted with Et_2O (300 ml in 6 portions). After being dried, the organic extracts were evaporated to give **26** (21.5 g, 85%) as a clear liquid.[15] TLC (CH_2Cl_2–acetone 4:1) $R_f = 0.45$. $[\alpha]_D^{25} + 64.5°$ ($c = 1$, MeOH). HPLC (RP): $R_t = 2.8$ min.

IR (film): 3300, 3150 (OH), 1440, 1320, 1270, 1160, 1070, 1040, 1000 cm^{-1}. ^{1}H-NMR (CD_3OD): δ 1.38 (2H, mc, CH_2, $C_{1'}$), 1.8–2.5 (3H, m, CH_2, CH, C_5, C_2), 3.22 (2H, t, J = 6 Hz, CH_2—O), 3.95 (1H, m, CH—O), 5.2 (2H, br s, CH=CH). MS: M^+ 128 (< 1), *m/e* 110 (75), 97 (8), 96 (32), 83 (35), 81 (100), 80 (61), 79 (83), 67 (69), 66 (66), 54 (49), 41 (88), 39 (51).

(+)-2β-(2-*Trityloxy-ethyl*)-3-*cyclopenten*-1β-*ol* (**20d**)

To a stirred soln of **26** (12.8 g, 0.1 mol) in dry pyridine (150 ml) at room temp was added trityl chloride (33.4 g, 0.12 mol), and the mixture was stirred for 3hr at 50°. After cooling, the mixture was filtered, evaporated *in vacuo* and redissolved in hexane (100 ml). The insoluble triphenylcarbinol was filtered off, and the filtrate evaporated *in vacuo* to give crude product, which was purified by column chromatography to provide **20d** (16.8 g, 45.4%) as a clear oil. TLC (benzene–acetone 10:1) R_f = 0.35. HPLC (RP): $R_t = 16.4$ min. $[\alpha]_D^{25} + 36°$ (c = 1, benzene). IR (film): 3400, 3050, 1605, 1505, 1460, 1320, 1270, 1225, 1155, 1075, 1040 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.85 (2H, m, CH_2, $C_{1'}$), 2.4 (3H, m, CH_2, CH, C_5, C_1), 3.25 (2H, t, J = 6 Hz, CH_2—O), 4.3 (1H, m, CH—O), 5.5 (2H, m, CH=CH), 7.2 (15H, m, aromatic protons).

(+)-3,4-β-*Epoxy*-2β-(2-*trityloxy-ethyl*)-*cyclopentan*-1β-*ol* (**21d**)

To a stirred soln of **20d** (10.8 g, 0.029 mol) and vanadyl acetylacetonate (0.1 g) in dry benzene (100 ml), there was added dropwise freshly prepared t-butyl hydroperoxide (9 g, 0.1 mol), and the resulting soln was refluxed for 1 hr. The soln was cooled to room temp, filtered through a short column packed with silica gel, using benzene–acetone 10:1 as eluent, to obtain **21d** (10 g, 96%) as a clear oil. TLC (benzene–acetone 10:1) R_f = 0.3. HPLC (RP): $R_t = 11.6$ min. $[\alpha]_D^{25} + 22°$ ($c = 1$, MeOH).

IR (film): 3350 (OH), 1605, 1505, 1460, 1425, 1380, 1330, 1200, 1090, 1070, 1065 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.85 (2H, m, CH_2, $C_{1'}$), 2.05 (3H, mc, CH_2, CH, C_5, C_1), 3.3 (4H, mc, CH_2—O, 2CH—O), 3.8 (1H, m, CH—O), 7.2 (15H, m, aromatic protons).

(+)-3,4-β-*Epoxy*-2β-(2-*trityloxy-ethyl*)-*cyclopentanone* (**22d**)

Epoxycyclopentanol **21d** (10.8 g, 0.028 mol) was oxidized with pyridinium dichromate (21.1 g, 0.056 mol), as described for **22b** to obtain **22d** in 92% yield. Op.: 123–124°. TLC (benzene–MeOH 10:1) $R_f = 0.75$. HPLC (RP): $R_t = 10.8$ min. $[\alpha]_D^{25} + 32°$ ($c = 1$, MeOH).

IR (film): 3040, 1745 (CO), 1600, 1500, 1460, 1405, 1260, 1230, 1145, 1090, 1070, 1030 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.9 (2H, m, CH_2, $C_{1'}$), 2.5 (3H, m, CH_2, CH, C_5, C_1), 3.3 (2H, t, J = 6 Hz, CH_2—O), 3.65 (2H, m, 2CH—O), 7.3 (15H, m, aromatic protons). MS: M^+ 384 (3), *m/e* 307 (5), 259 (23), 243 (100), 165 (40), 141 (12), 125 (35), 105 (27), 77 (14), 55 (12).

S,S-(+)-4-*Hydroxy*-5-(2-*trityloxy-ethyl*)-2-*cyclopentenone* (**23d**)

With the procedure described previously for the preparation of **23b**, **23d** was prepared in 98% yield from **22d**. TLC (benzene–MeOH 10:1) $R_f = 0.4$. HPLC (RP): $R_t = 8$ min. $[\alpha]_D^{25} + 41°$ ($c = 1$, MeOH).

IR (film): 3350 (OH), 3040, 1710 (CO), 1650 (C=C), 1590, 1500, 1460, 1340, 1210, 1170, 1070, 1030 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.9–2.4 (3H, m, CH_2, CH, $C_{1'}$, C_1), 3.25 (2H, t, J = 6 Hz, CH_2—O), 4.65 (1H, m, CH—O), 6.05 (1H, m, =CH), 7.25 (16H, m, aromatic protons, =CH).

S-(−)-4-*Hydroxy*-2-(2-*trityloxy-ethyl*)-2-*cyclopentenone* (**24h**)

Following the procedure described previously for the synthesis of **24c**, **24h** was prepared in 56% yield from **23d**. TLC (benzene–acetone 10:1). $R_f = 0.25$. HPLC (RP): $R_t = 6$ min. $[\alpha]_D^{25} - 8.7°$ ($c = 1$, MeOH). Op.: 103–104°.

IR (film): 3350 (OH), 3040, 1710 (CO), 1635 (C=C), 1590, 1500, 1460, 1320, 1210, 1150, 1070, 1040 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.9–2.7 (4H, m, $2CH_2$), 3.25 (2H, t, J = 6 Hz, CH_2—O), 4.75 (1H, m, CH—O), 7.25 (16H, m, aromatic protons, =CH).

t-Butyldimethylsilyl derivative (**24i**). Compound **24h** was protected with t-butyldimethylsilyl chloride as above to give **24i** (87% yield). TLC (benzene–acetone 10:1). $R_f = 0.9$. $[\alpha]_D^{25}$ $-6.2°$ ($c = 1$, MeOH).

IR (film): 3040, 1710 (CO), 1590, 1500, 1470, 1460, 1380, 1245, 1160, 1080, 1010 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 0.05 (6H, s, $2CH_3$, Si—CH_3), 0.8 [9H, br s, $3CH_3$, $C(CH_3)_3$], 2.15–2.6 (4H, m, $2CH_2$, C_5, $C_{1'}$), 3.15 (2H, t, J = 6 Hz, CH_2—O), 4.75 (1H, m, CH—O), 7.2 (16H, m, aromatic protons, =CH). MS: M^+ 498 (< 1), *m/e* 255 (35), 242 (100), 239 (12), 228 (3), 188 (7), 164 (24), 147 (20), 123 (13), 75 (26), 73 (30).

REARRANGEMENTS OF CYCLOPENTENONES

Methyl-7-(3-*methoxy*-5-*oxo*-1-*cyclopentenyl*)-5(Z)-*heptenoate* (**7b**), *methyl* 7-(4-*methoxy*-2-*oxo*-3-*cyclopentyl*-5(Z)-*heptenoate* (**9b**), *and methyl* 7-(2-*methoxy*-5-*oxo*-1-*cyclopentyl*)-5(Z)-*heptenoate* (**11b**)

To a stirred cooled (0°) soln of NaOMe (obtained from 0.1 g of Na, 4.35 mmol) in dry MeOH (10 ml) was added **1b** (1.0 g, 2.84 mmol) and the mixture was stirred at room temp for 1 hr, under agron. The mixture was diluted with water (4 ml) and extracted with Et_2O (6 × 15 ml). The combined organic extracts were washed with brine and dried. Removal of the solvent *in vacuo* afforded an oily residue (0.6 g) which was separated by column chromatography (benzene–EtOAc 3:2), to give **7b** (0.32 g, 44.7%) as an oil (a mixture of *R* and *S* enantiomers, ratio 74:26) **9b** (0.03 g, 4.2%) as a yellow oil, and **11b** (0.15 g, 21.4%) as a yellow oil.

Compound **7b**. TLC (benzene–EtOAc 3:2). $R_f = 0.68$. $[\alpha]_D^{25}$ $+5.4°$ ($c = 1$, MeOH). (Found: C, 66.92; H, 8.05. $C_{14}H_{20}O_4$ requires: C, 66.67, H, 7.94%.) IR (film): 1730, 1720 (C=O), 1630 (C=C), 1450, 1350, 1240, 1180, 1150, 1100, 1045, 1000 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.65 (2H, m, CH_2, C_3), 1.95–2.6 (6H, m, $3CH_2$, C_2, C_4, $C_{4'}$), 2.9 (2H, mc, CH_2, C_7), 3.38 (3H, s, OCH_3, $C_{3'}$), 3.65 (3H, s, OCH_3, C_1), 4.45 (1H, mc, CH—O), 5.45 (2H, mc, CH=CH), 7.15 (1H, mc, C=CH).

Decoupling experiment: Selective irradiation of the C-1 protons (δ 2.9) resulted sharpening at δ 5.45 (2-H/3-H) and changed the C-3′ proton resonance to a doublet (δ 7.15, J = 2.5 Hz). Selective decoupling of 3′-H (δ 7.15) greatly simplified the methine and methylene resonances (δ 4.45 and 2.9, respectively). Selective decoupling of the C-4′ proton (δ 4.45) changed the C-3′ proton resonance to a triplet (J = 1.5 Hz) and also affected the resonance due to C-4 protons (δ 2.2–2.6).

MS: M^+ 252 (2), *m/e* 220 (100), 189 (28), 188 (32), 160 (47), 146 (53), 133 (42), 119 (53), 94 (48), 91 (43), 79 (25), 67 (24).

Compound **9b**. TLC (benzene–EtOAc 3:2) $R_f = 0.4$.

(Found: C, 66.74, H, 7.68. $C_{14}H_{20}O_4$ requires: C, 66.67, H, 7.94%.) IR (film): 1730, 1690 (CO), 1590 (C=C), 1460, 1450, 1360, 1250, 1180, 1155, 1070, 1040 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.6 (2H, mc, CH_2, C_3), 2.0–2.75 (8H, m, $4CH_2$, C_2, C_4, $C_{3'}$, $C_{4'}$), 2.8 (2H, d, J = 5 Hz, CH_2, C_7), 3.68 (3H, s, OCH_3, C_1), 3.9 (3H, s, OCH_3, $C_{2'}$), 5.25 (1H, br s, CH=C), 5.32 (2H, mc, CH=CH). MS: M^+ 252 (6), *m/e* 221 (6), 164 (4), 151 (7), 112 (100), 97 (6), 79 (5), 55 (6).

Compound **11b**. TLC (benzene–EtOAc 3:2). R_f = 0.32. (Found: C, 66.97; H, 8.05. $C_{14}H_{20}O_4$ requires: C, 66.67; H, 7.94%.) IR (film): 1730, 1685 (C=O), 1615 (C=C), 1460, 1450, 1360, 1250, 1190, 1160, 1100, 1080, 1040 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.6 (2H, m, CH_2, C_3), 2.25 (9H, mc, $4CH_2$, C_2, C_4, C_7, $C_{5'}$, CH), 3.65 (3H, s, OCH_3, C_1), 3.82 (3H, s, OCH_3, $C_{4'}$), 5.4 (2H, mc, CH=CH). MS: M^+ 252 (32), *m/e* 221 (22), 220 (17), 179 (32), 165 (22), 164 (18), 151 (16), 125 (100), 91 (17), 79 (13), 67 (18), 55 (15).

Trimer of hydroxycyclopentenone (**40a**)

To a stirred cooled (0°) soln of NaOMe (obtained from 0.1 g of Na, 4.3 mmol) in dry MeOH (15 ml) was added **1a** (1.75 g, 7.3 mmol) and the mixture was stirred at 0° for 12 hr, under argon. The mixture was concentrated *in vacuo* and the residue was taken up in CH_2Cl_2 (40 ml). The soln was washed with water (10 ml), dried and then evaporated *in vacuo* to give an oily residue, which was separated by column chromatography (benzene–EtOAc 4:1) affording **7b** (0.61 g, 34.9%), **9b** (0.07 g, 4%), **11b** (0.27 g, 15.4%) and **40a** (0.4 g, 22.9%) as a yellow oil.

Compound **40a**. TLC (benzene–EtOAc 3:2) R_f = 0.55. (Found: C, 68.82; H, 7.11. $C_{19}H_{50}O_{10}$ requires: C, 69.03; H, 7.37%.) IR (film): 3420, 1725, 1715, 1710, 1700 (CO), 1640, 1630 (C=C), 1460, 1450, 1360, 1240, 1185, 1160, 1130, 1100, 1045, 1000 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.66 (6H, m, $3CH_2$, C_3), 1.9–2.7 (20H, m, $8CH_2$, 4CH, C_2, C_4, C_7, $C_{1''}$, $C_{5'}$, $C_{3''}$, $C_{4''}$, $C_{3'''}$), 2.9 (4H, m, $2CH_2$, C_7), 3.63 (9H, s, $3OCH_3$), 4.25 (1H, mc, O—CH), 5.35 (6H, m, CH=CH, $C_{5,6}$), 5.94 (1H, dm, J = 2 Hz, CH=C, $C_{3'}$), 7.2 (1H, br s, C=CH, $C_{5''}$), 7.35 (1H, dm, J = 2 Hz, C=CH, $C_{4'}$). MS: M^+ 678 (32), *m/e* 660 (2) [$M-H_2O$], 647 (21) [$M-OCH_3$], 646 (9), 539 (54) [$M-C_8H_{12}O_2$, $C_{1''-7}$], 519 (12), 506 (14), [$M-C_8H_{12}O_2-OCH_3$], 440 (13), 405 (10), 247 (26), 207 (15), 173 (20), 159 (20), 145 (27), 91 (48), 81 (100), 67 (90), 55 (67).

Ethyl 7 - (3 - *ethoxy* - 5 - *oxo* - 1 - *cyclopentenyl*) - 5(Z) - *heptenoate* (**7c**), (±) - *ethyl* 7 - (4 - *ethoxy* - 2 - *oxo* - 3 - *cyclopentenyl*) - 5(Z) - *heptenoate* (**9c**), *and ethyl* 7 - (2 - *ethoxy* - 5 - *oxo*-1-*cyclopentenyl*)-5(Z)-*heptenoate* (**11c**)

To a stirred cooled (0°) soln of NaOEt (prepared from 0.1 g Na, 4.3 mmol) in dry EtOH (10 ml) was added **1g** (1.0 g, 2.7 mmol) and the resulting mixture was stirred at room temp for 2 hr, under argon. The mixture was poured into water (20 ml) and extracted with Et_2O (6 × 30 ml). The combined ethereal extracts were dried, concentrated *in vacuo*, and the oily residue (0.75 g) was separated by column chromatography (benzene–EtOAc 3:2) to give **7c** (0.33 g, 43.6%) as a light yellow oil (a mixture of *R* and *S* enantiomers, ratio 80:20), **9c** (0.027 g, 3.5%) as a yellow oil, and **11c** (0.18 g, 23.4%) as a yellow oil.

Compound **7c**. TLC (benzene–EtOAc) R_f = 0.79. $[\alpha]_D^{25}$ +6.76° (*c* = 0.74, MeOH). ^{1}H-NMR ($CDCl_3$): δ 1.15 (6H, t, J = 6 Hz, $2CH_3$), 1.65 (2H, mc, CH_2, C_3), 1.85–2.7 (6H, m, $3CH_2$, C_2, C_4, $C_{4'}$), 2.85 (2H, mc, CH_2, C_7), 3.5 (2H, q, J = 6 Hz, CH_2—O, $C_{3'}$), 4.05 (2H, q, J = 6 Hz, CH_2—O, C_1), 4.45 (1H, mc, CH—O), 5.4 (2H, mc, CH=CH), 7.1 (1H, mc, CH=C). MS: M^+ 280 (4), *m/e* 235 (21), 234 (28), 189 (21), 188 (20), 160 (36), 146 (36), 133 (21), 132 (11), 119 (34), 117 (13), 107 (15), 105 (17), 94 (91), 91 (40), 79 (30), 77 (26), 67 (30), 43 (44), 41 (47), 29 (100), 27 (40).

Compound **9c**. TLC (benzene–EtOAc 3:2) R_f = 0.46. ^{1}H-NMR ($CDCl_3$): δ 1.25 (3H, t, J = 6 Hz, CH_3, C_1), 1.42 (3H, t, J = 6 Hz, CH_3, $C_{4'}$), 1.6 (2H, mc, CH_2, C_3), 2.0–2.65 (9H, m, $4CH_2$, C_2, C_4, C_7, $C_{5'}$, CH), 4.05 (2H, q, J = 6 Hz, CH_2—O, C_1), 4.15 (2H, q, J = 6 Hz, CH_2—O, $C_{4'}$), 5.3 (1H, br s, CH=C), 5.42 (2H, mc, CH=CH). MS: M^+ 280 (15), *m/e* 235 (13), 179 (29), 165 (3), 156 (2), 139 (4), 126 (100), 98 (23), 69 (8), 29 (3).

Compound **11c**. TLC (benzene–EtOAc 3:2). R_f = 0.32. ^{1}H-NMR ($CDCl_3$): δ 1.23 (3H, t, J = 6 Hz, CH_3, C_1), 1.3 (3H, t, J = 6 Hz, CH_3, $C_{2'}$), 1.7 (2H, mc, CH_2, C_3), 1.95–2.7 (8H, m, $4CH_2$, C_2, C_4, $C_{3'}$, $C_{4'}$), 2.85 (2H, d, J = 6 Hz, CH_2, C_7), 4.05 (2H, q, J = 6 Hz, CH_2—O, C_1), 4.18 (2H, q, J = 6 Hz, CH_2—O, $C_{2'}$), 5.32 (2H, mc, CH=CH). MS: M^+ 280 (86), *m/e* 235 (51), 234 (38), 193 (50), 179 (18), 178 (23), 163 (20), 156 (16), 151 (18), 139 (88), 111 (100), 99 (19), 98 (19), 95 (22), 79 (18), 67 (20), 55 (46), 43 (30), 41 (32), 29 (67).

4 - *Methoxy* - 2 - [2(Z) - *pentenyl*] - 2 - *cyclopentenone* (**31b**) *and* (±)-3-*methoxy*-5-[2(Z)-*pentenyl*]-2-*cyclopentenone* (**33b**)

To a cooled (0°) soln of NaOMe [prepared from 1.2 g (0.053 mol) of Na and dry MeOH (15 ml)] was added **24b** (1.5 g, 0.0054 mol), and the resulting soln was stirred at 0° for 10 min, then at 25° for 1.5 hr. The mixture was filtered through a short column, washed with CH_2Cl_2, the solvent was evaporated *in vacuo*, and the residue was chromatographed with CH_2Cl_2 to give **31b** (0.8 g, 83%) as an oil, and **33b** (0.1 g, 10%) as an oil, and **35b** (0.02 g, 2%).

Compound **31b**. TLC (benzene–acetone 10:1). R_f = 0.68. HPLC (RP): R_t = 5.6 min., (SP) R_t = 8.1 min.

IR (film): 1720 (CO), 1640 (C=C), 1470, 1420, 1380, 1360, 1300, 1270, 1190, 1105, 1050, 1000 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 0.98 (3H, t, J = 6 Hz, CH_3), 1.85–2.6 (4H, m, $2CH_2$, C_3, $C_{4'}$), 2.85 (2H, m, CH_2, $C_{1'}$), 3.25 (3H, s, OCH_3), 4.3 (1H, m, CH—O), 5.3 (2H, m, CH=CH), 7.0 (1H, m, =CH). MS: M^+ 180 (92), *m/e* 165 (17), 151 (53), 148 (39), 133 (55), 119 (100), 109 (33), 107 (23), 105 (31), 91 (81), 79 (48), 77 (38), 55 (49).

Compound **33b**. TLC (benzene–acetone 10:1) R_f = 0.32. IR (film): 1700 (CO), 1610 (C=C), 1465, 1440, 1365, 1300, 1240, 1160, 1000 cm^{-1}. ^{1}H-NMR (CCl_4): δ 0.96 (3H, t, J = 6 Hz, CH_3), 1.8–2.6 (7H, m, $3CH_2$, CH, C_4, $C_{1'}$, $C_{4'}$, C_5), 3.78 (3H, s, OCH_3), 5.12 (1H, br s, =CH), 5.3 (2H, m, CH=CH). MS: M^+ 180 (26), *m/e* 165 (7), 150 (34), 125 (8), 112 (100), 97 (12), 75 (14), 69 (15).

Compound **35b**. TLC (benzene–acetone 10:1) R_f = 0.27. IR (film): 1695 (CO), 1600 (C=C), 1460, 1440, 1380, 1360, 1310, 1240, 1155, 1100, 1040, 1000 cm^{-1}. ^{1}H-NMR (CCl_4): δ 0.95 (3H, t, J = 6 Hz, CH_3), 1.8–2.55 (6H, m, $3CH_2$, C_4, C_5, $C_{4'}$), 2.84 (2H, m, CH_2, $C_{1'}$), 3.9 (3H, s, OCH_3), 5.35 (2H, m, CH=CH).

4-*Methoxy*-2-[2(Z)-*pentenyl*]-2-*cyclopentenone* (**31b**)

Silyl ether **24e** (0.5 g, 1.5 mmol) was added to a stirred soln of NaOMe, prepared from 0.035 g (1.5 mmol) of Na and dry MeOH (5 ml), at 0°. The deep red soln was left at 0° for 3 hr and then filtered through a short column. The solvent was evaporated *in vacuo* and the residue was chromatographed to give **31b** (0.23 g, 85.2%, a mixture of *R* and *S* isomers, ratio 47:53). $[\alpha]_D^{25}$ −1° (*c* = 1, MeOH).

4-*Ethoxy*-2-[2(Z)-*pentenyl*]-2-*cyclopentenone* (**31c**)

Silyl ether **24d** (0.8 g, 2.86 mmol) was added to a stirred and cooled (0°) soln of NaOMe (prepared from 0.1 g of Na and 5 ml of dry MeOH). The mixture was left to stand at room temp for 1 hr and then filtered through a short column. The solvent was evaporated *in vacuo* and the residue was chromatographed (silica gel, benzene–acetone 10:1) to give **31c** (0.37 g, 66.7%) as an oil, **33c** (0.03, 5.4%) as an oil and **35c** (0.015 g, 2.7%) as an oil.

Compound **31c** (a mixture of *R* and *S* isomer, ratio 36:64), TLC (CH_2Cl_2) R_f = 0.5. $[\alpha]_D^{25}$ −4.8° (*c* = 1, MeOH). IR (film): 1720 (CO), 1635 (C=C), 1460, 1420, 1360, 1300, 1260, 1185, 1100 cm^{-1}. ^{1}H-NMR (CCl_4): δ 0.96 (3H, t, J = 6 Hz, CH_3, $C_{5'}$), 1.1 (3H, t, J = 6 Hz, CH_3), 2.0–2.55 (4H, m, $2CH_2$, C_5, $C_{4'}$), 2.85 (2H, m, CH_2, $C_{1'}$), 3.45 (2H, q, J = 6 Hz, O—CH_2), 4.35 (1H, m, CH—O), 5.35 (2H, m, CH=CH), 7.0 (1H, m, =CH). MS: M^+ 194 (36), *m/e* 180 (9), 165 (44), 151 (14), 148 (41), 137 (38), 133 (41), 123 (25), 121 (32), 119 (64), 91 (73), 55 (59), 43 (100), 41 (94).

Compound **33c**. TLC (CH_2CH_2) R_f = 0.25. IR (film): 1695 (CO), 1635 (C=C), 1470, 1385, 1360, 1260, 1200, 1130, 1080,

1050 cm^{-1}. MS: M^+ 194 (62), *m/e* 180 (43), 165 (48), 151 (35), 139 (50), 137 (27), 127 (25), 125 (58), 111 (100).

Compound **35c**. TLC (CH_2Cl_2) R_f = 0.15. IR (film): 1695 (CO), 1620 (C=C), 1460, 1440, 1380, 1360, 1250, 1200, 1140, 1070, 1030 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 0.95 (3H, t, J = 6 Hz, CH_3, $C_{5'}$), 1.25 (3H, t, J = 6 Hz, CH_3), 2.05–2.7 (6H, m, $3CH_2$), 4.2 (2H, q, J = 6 Hz, O—CH_2), 5.35 (2H, m, CH=CH). MS: M^+ 194 (62), *m/e* 180 (43), 165 (48), 151 (35), 139 (50), 137 (27), 127 (25), 125 (58), 111 (100).

4-Methoxy-2-pentyl-2-cyclopentenone (**31d**) *and* (±)-*3-methoxy-5-pentyl-2-cyclopentenone* (**33d**)

Silyl ether **24g** (1.0 g, 3.5 mmol) was added to a stirred soln of NaOMe, prepared from 0.082 g (3.5 mmol) of Na and dry MeOH (5 ml), at 20°. The deep red soln was left at room temp for 3.5 hr and then filtered through a short column. The solvent was evaporated *in vacuo* and the residue was chromatographed (silica gel, benzene–acetone 10:1) to give **31d** (0.50 g, 78%) as a clear oil, and **33d** (0.01 g, 1.5%) as pale yellow oil.

Compound **31d**. TLC (benzene–acetone 10:1) R_f = 0.72. HPLC (RP): R_t = 4.8 min. $[\alpha]_D^{25}$ – 3.75° (*c* = 1, MeOH). IR (film): 1710 (CO), 1635 (C=C), 1460, 1410, 1380, 1355, 1250, 1190, 1100, 1065, 1000 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 0.87 (3H, t, J = 6 Hz, CH_3), 1.32 (6H, m, $3CH_2$, $C_{2'-4'}$), 2.05–2.7 (4H, $2CH_2$, C_5, $C_{1'}$), 3.38 (3H, s, OCH_3), 4.45 (1H, m, CH—O), 7.14 (1H, m, =CH). MS: M^+ 182 (100), *m/e* 167 (10), 153 (40), 150 (33), 139 (16), 137 (17), 125 (36), 111 (42), 95 (56), 75 (61), 67 (41).

Compound **33d**. TLC (benzene–acetone 10:1) R_f = 0.35. HPLC (RP): R_t = 4.4 min. IR (film): 1690 (C=O), 1600 (C=C), 1460, 1435, 1360, 1290, 1240, 1190, 1160, 1120, 1105, 1000 cm^{-1}. ^{1}H-NMR (CCl_4): δ 0.9 (3H, t, J = 6 Hz, CH_3), 1.3 (8H, m, $4CH_2$, $C_{2'-4'}$), 2.15–2.6 (3H, m, CH_2, CH, C_4, C_5), 3.78 (3H, s, OCH_3), 5.1 (1H, br s, =CH). MS: M^+ 182 (9), *m/e* 166 (5), 137 (11), 125 (21), 112 (100), 97 (9), 69 (7).

4-Methoxy-2-pentyl-2-cyclopentenone (**31d**)

Silyl ether **24g** (1.0 g, 3.5 mmol) was added to a cooled (–20°) stirred soln of NaOMe (0.19 g, 3.5 mmol) in dry MeOH (5 ml) and the resultant soln was kept at –20° for 3 hr. The mixture was filtered through a short silica gel column, the solvent was evaporated *in vacuo* and the residue was chromatographed (silica gel, benzene–acetone 10:1) to give **31d** (0.57 g, 89.5%). $[\alpha]_D^{25}$ + 7° (*c* = 1, MeOH) a mixture of *R* and *S* isomers, ratio 76:24.

4-Methoxy-2-(2-trityloxy-ethyl)-2-cyclopentenone (**31e**), (±)-*3-methoxy-5-(2-trityloxy-ethyl)-2-cyclopentenone* (**33e**), *and 3-methoxy-2-(2-trityloxy-ethyl)-2-cyclopentenone* (**35e**)

Silyl ether **24i** (0.8 g, 1.6 mmol) was added to a stirred soln of NaOMe, prepared from Na (0.037 g, 1.6 mmol) and dry MeOH (5 ml), at 20°. The resulting red soln was stirred at 25° for 6 hr and then filtered through a short column. After removal of the solvent, the residue was chromatographed (silica gel, benzene–acetone 10:1) to give **31e** (0.32 g, 50%) as an oil, **33e** (0.04 g, 6%) as a pale yellow oil, and **35e** (0.22 g, 34%) as a solid.

Compound **31e**. TLC (benzene–acetone 10:1) R_f = 0.75. HPLC (RP): R_t = 9.6 min. $[\alpha]_D^{25}$ + 0.9° (*c* = 1, MeOH), a mixture of *R* and *S* enantiomers, ratio 53:47. IR (film): 3040, 1710 (CO) 1640 (C=C), 1595. 1500, 1460, 1410, 1355, 1240, 1210, 1190, 1160, 1090, 1040, 1000 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.2–2.7 (4H, m, $2CH_2$, C_5, $C_{1'}$), 3.22 (2H, t, J = 6 Hz, CH_2—O), 3.34 (3H, s, OCH_3), 4.45 (1H, m, CH—O), 7.3 (16H, m, aromatic protons, =CH). MS: M^+ 398 (< 1), *m/e* 259 (11), 243 (100), 165 (51), 155 (81), 139 (61), 123 (15), 105 (36), 95 (17), 79 (14), 77 (28).

Compound **33e**. TLC (benzene–acetone 10:1) R_f = 0.5. HPLC (RP): R_t = 7.6 min. IR (film): 3040, 1690 (CO), 1590 (C=C), 1500, 1485, 1460, 1360, 1300, 1240, 1180, 1160, 1080, 1040, 1000 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.3 (2H, br s, CH_2, $C_{1'}$), 2.2–2.8 (3H, m, CH_2, CH, C_4, C_5), 3.22 (2H, t, J = 6 Hz, CH_2—O), 3.78 (3H, s, OCH_3), 5.25 (1H, br s, =CH, C_2), 7.3 (16H, m, aromatic protons, =CH). MS: M^+ 398 (< 1), *m/e* 243 (32), 165 (31), 155 (100), 139 (38), 123 (9), 95 (3), 79 (5), 77 (12).

Compound **35e**. Op.: 163–169°. TLC (benzene–acetone 10:1) R_f = 0.4. HPLC (RP): R_t = 8.4 min. IR (KBr): 3040, 1685 (CO), 1615 (C=C), 1500, 1460, 1360, 1270, 1250, 1220, 1160, 1120, 1060, 1040, 1010 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.3–2.7 (6H, m, $3CH_2$, C_4, C_5, $C_{1'}$), 3.2 (2H, t, J = 6 Hz, CH_2—O), 3.86 (3H, s, OCH_3), 7.4 (15H, m, aromatic protons). MS: M^+ 398 (< 1), *m/e* 243 (44), 165 (44), 155 (100), 139 (18), 105 (9), 95 (4), 79 (6), 77 (14).

Reaction of R,R-(–)-*methyl 7-(5-hydroxy-2-oxo-3-cyclopenten-1-yl)-5(Z)-heptenoate* (**18**, R^1 = CH_3) *with sodium methoxide*

To a stirred soln of NaOMe (0.54 g, 10 mmol) in dry MeOH (5 ml) was added **18** (R^1 = CH_3) 1.12 g, 5 mmol). The resultant soln was stirred at room temp for 1 hr and then filtered through a short silica gel column. Evaporation of the solvent *in vacuo* afforded a yellow liquid, which was chromatographed to yield **7b** (0.46 g, 38.7%, a mixture of *R* and *S* enantiomers, ratio 60:40), **9b** (0.08 g, 6.7%) and **11b** (0.32 g, 26.9%).

Reaction of S,S-(+)-*methyl* [7-(5-*hydroxy*-2-*oxo*-3-*cyclopentenyl*)]-5(Z)-*heptenoate* (**23a**, R^1 = CH_3) *with sodium methoxide*

To a stirred soln of NaOMe (0.54 g, 10 mmol) in dry MeOH (5 ml) was added **23b** (1.12 g, 5 mmol). After stirring for 1 hr at room temp, the mixture was filtered through a short silica gel column. The solvent was removed *in vacuo*, yielding an oil, which was chromatographed (benzene–EtOAc 3:2) to afford **7b** (0.485 g, 40.7%, a mixture of *R* and *S* enantiomers, ratio 43:57), **9b** (0.12 g, 10%) and **11b** (0.3 g, 25.2%).

The reaction of the t-butyldimethylsilyl ether of **23b** with NaOMe (2 equiv) at room temp (2 hr) yielded **7b** (42%), **9b** (5.2%) and **11b** (14%), and at 0° (2 hr) afforded **7b** (54%), **9b** (2.8%) and **11b** (5.7%).

Reaction of S,S-(–)-*4-hydroxy-5-[2(Z)-pentenyl]-2-cyclopentenone* (**23b**) *with sodium methoxide*

To a stirred soln of NaOMe (0.32 g, 6 mmol) in dry MeOH (3 ml) was added **23b** (1 g, 6 mmol). The reaction was stirred at room temp for 0.5 hr and then filtered through a short column. Evaporation of the solvent *in vacuo* afforded **31b** (0.75 g, 69.4%, mixture of *R* and *S* enantiomers, ratio 44:56).

Isomerization of methyl 7-(3-methoxy-5-oxo-1-cyclopentenyl)-5(Z)-heptanoate (**7b**)

To a stirred soln of NaOMe (0.24 g, 4.3 mmol) in dry MeOH (10 ml) was added **7b** (0.63 g, 2.5 mmol) and the soln was stirred at room temp for 72 hr. The mixture was filtered through a short silica gel column, the solvent was evaporated *in vacuo* and the oily residue was chromatographed to afford **9b** (0.32 g, 53.8%).

Isomerization of 4-methoxy-2-[2(Z)-pentyl]-2-cyclopentenone (**31b**)

To a cooled (0°) soln of NaOMe (0.7 g, 0.013 mol) in dry MeOH (20 ml) was added **31b** (0.9 g, 0.005 mol), and the resulting soln was stirred at room temp for 48 hr. The mixture was filtered through a short column, the solvent was evaporated *in vacuo*, and the residue was chromatographed with CH_2Cl_2 to give **33b** (0.54 g, 60%).

Isomerization of 4-methoxy-2-pentyl-2-cyclopentenone (**31d**)

To a soln of NaOMe (0.24 g, 4.3 mmol) in dry MeOH (5 ml) was added **31d** (0.2 g, 1.1 mmol), and the resulting red soln was stirred at room temp for 72 hr. The mixture was filtered through a short silica gel column, the solvent was evaporated *in vacuo*, and the residue was chromatographed with benzene–acetone (10:1) to give **33d** (0.13 g, 62%).

Isomerization of 4-methoxy-2-(2-trityloxy-ethyl)-2-cyclopentenone (**31e**)

To a soln of NaOMe (0.24 g, 4.3 mmol) in dry MeOH was added derivative **31e** (0.2 g, 0.5 mmol), and the red soln was

stirred at room temp for 96 hr. The work up and chromatography as above gave **33e** (0.15 g, 75%).

Dimerization of cyclopentenone **1b** (**17b**)

To a cooled soln of diisopropylamine (0.12 g, 1.2 mmol) in dry THF (3 ml) was added n-BuLi (0.7 ml, 1.3 mmol 1.9 M soln in n-hexane). After the reaction was stirred at 0° for 30 min, the mixture was cooled to −78° and a soln of **1b** (0.35 g, 1 mmol) in dry THF (3 ml) was slowly added, and the resulting soln was maintained at −78° for 2 hr. The mixture was quenched with water (3 ml), extracted with CH_2Cl_2 (4 × 10 ml), washed with water, dried and then concentrated *in vacuo*. The oily residue was separated by chromatography (hexane–acetone 7:3) to yield 0.11 g (31.4%) of **17b** as a yellow oil. IR (film): 1735, 1715 (CO), 1640 (C=C), 1470, 1445, 1360, 1250, 1160, 1070, 900, 830, 780 cm^{-1}. ^{1}H-NMR (CCl_4): δ 0.1 [6H, s, $(CH_3)_2Si$], 0.15 [6H, s, $(CH_3)_2Si$], 0.94 [9H, s, $(CH_3)_3C$], 0.96 [9H, s, $(CH_3)_3C$], 1.65 (4H, m, $2CH_2$, C_3), 1.8–2.7 (15H, m, $6CH_2$, 3CH, C_2, C_4, C_7, $C_{4'}$, $C_{1'}$, $C_{2'}$, $C_{4''}$), 3.0 (2H, m, CH_2, C_7), 3.7 (3H, s, OCH_3), 3.78 (3H, s, OCH_3), 4.55 (1H, m, CH—O, $C_{3'}$), 4.9 (1H, m, CH—O, $C_{3''}$), 5.5 (4H, m, CH=CH), 7.05 (1H, m, C=CH). MS: M^+ 704 (< 1), *m/e* 647 (3) [M − $(CH_3)_3C$], 557 (12), 424 (3), 295 (10), 263 (3), 220 (3), 189 (7), 161 (3), 147 (3), 133 (4), 119 (4), 75 (100), 73 (17).

Dimerization of cyclopentenone **24g** (**42c**)

To a cooled (−20°) soln of diisopropylamine (0.12 g, 1.2 mmol) in dry THF (5 ml) was added n-BuLi (0.7 ml, 1.3 mmol, 1.9 M soln in n-hexane). After being stirred at 0° for 30 min, the mixture was cooled to −78° and a soln of **24g** (0.28 g, 1 mmol) in dry THF (3 ml) was added, and the resulting soln was kept at −78° for 2 hr. The mixture was quenched with water (3 ml), extracted with CH_2Cl_2 (4 × 10 ml), washed with water, dried and then concentrated *in vacuo*. The oily residue was purified by chromatography (hexane–acetone 5:1) to yield **42c** (0.12 g, 42.5%), as a yellow oil. IR (film): 1730, 1710 (CO), 1640 (C=C), 1460, 1380, 1370, 1255, 1100, 1070, 1030, 940, 910, 840, 780 cm^{-1}. ^{1}H-NMR (CCl_4): δ 0.05 [12H, m, $(CH_3)_2Si$], 0.85 [24H, m, $2CH_3$, $(CH_3)_3C$], 1.4 (16H, m, $8CH_2$), 2.3 (5H, m, 3CH, CH_2), 4.4 (1H, mc, CH—O), 5.1 (1H, mc, CH—O), 6.95 (1H, mc, C=CH). MS: M^+ 564 (< 1), *m/e* 507 (12), 436 (9), 433 (10), 376 (57), 325 (3), 323 (3), 294 (2), 267 (3), 225 (20), 191 (22), 169 (29), 75 (100), 73 (37).

Trimerization of cyclopentenone **1b** (**40b**)

To a stirred cooled (0°) soln of t-BuOK (0.27 g, 2.8 mmol) in dry t-BuOH (5 ml) was added **1b** (1.0 g, 2.8 mmol) and the soln was stirred at 0° for 10 hr. The mixture was filtered through a short column, evaporated and then the residue was taken up in CH_2Cl_2. The soln was washed with water, dried and then evaporated *in vacuo* to give an oily residue, which was separated by chromatography (benzene–EtOAc 5:0.4) yielding **40b** (0.19 g, 25.7%) as a yellow oil. TLC (benzene–EtOAc 5:0.4) R_f = 0.45. IR (film): 1735, 1710, 1700 (CO), 1635, 1630 (C=O), 1460, 1440, 1380, 1360, 1250, 1220, 1180, 1160, 1130, 1100, 1050, 1020 cm^{-1}. ^{1}H-NMR (CCl_4): δ 0.05 (6H, br s, 2Si—CH_3), 0.85 [9H, br s, $C(CH_3)_3$], 1.9–2.7 (26H, m, $11CH_2$, 4CH), 2.85 (4H, m, $2CH_2$, C_7), 3.6 (9H, br s, $30CH_3$), 4.45 (1H, m, O—CH), 5.4 (6H, m, 3CH=CH), 6.05 (1H, m, CH=), 7.05 (1H, m, =CH), 7.4 (1H, m, =CH).

Trimerization of cyclopentenone (**45a** *and* **46a**)

To a stirred soln of t-BuOK (0.8 g, 7 mmol) in dry t-BuOH (10 ml) was added **24d** (1.1 g, 3.9 mmol) and the resulting soln was stirred at room temp for 3 hr. The mixture was concentrated *in vacuo* and the residue was taken up in CH_2Cl_2 (20 ml). The soln was washed with water and dried. Evaporation gave an oil which was purified by column chromatography (silica gel, CH_2Cl_2) to provide **45a** (0.25 g, 27%) as a pale yellow oil, and **46a** (0.22 g, 29%) as a yellow oil.

Compound **45a**. TLC (benzene–EtOAc 3:1) R_f = 0.6. IR (film): 1725, 1700 (CO), 1635 (C=C), 1460, 1410, 1380, 1360, 1240, 1200, 1150, 1060, 1000 cm^{-1}. ^{1}H-NMR (CCl_4): δ 0.08 (12H, m, $4CH_3$, Si—CH_3), 0.85 [27H, m, $2C(CH_3)_3$, $3CH_3$], 1.8–2.65 (14H, m, $5CH_2$, 4CH), 2.8 (4H, m, $2CH_2$, $C_{1'}$), 4.3 (1H, m, CH—O), 4.75 (1H, m, CH—O), 5.25 (6H, m, 3CH=CH), 6.85 (1H, m, =CH). MS: M^+ 708 (34), *m/e* 693 (2), 651 (27), 576 (52), 519 (20), 429 (8), 280 (21), 75 (50), 73 (100).

Compound **46a**. TLC (benzene–EtOAc 3:1) R_f = 0.45. IR (film): 1730, 1700 (CO), 1625 (C=C), 1460, 1440, 1380, 1360, 1300, 1240, 1100, 1060, 840 cm^{-1}. ^{1}H-NMR (CCl_4): δ 0.05 (6H, s, 2Si—CH_3), 0.9 [18H, m, $Si(CH_3)_3$, $3CH_3$], 1.6–2.6 (14H, m, $6CH_2$, 2CH), 2.85 (6H, m, $3CH_2$, $C_{1'}$), 4.7 (1H, m, CH—O), 5.35 (6H, m, 3CH=CH), 7.0 (1H, m, =CH). MS: M^+ 576 (< 1), *m/e* 535 (3), 521 (4), 520 (10), 519 (25), 371 (4), 223 (4), 173 (3), 129 (7), 105 (5), 91 (13), 79 (10), 77 (11), 75 (100), 73 (30), 69 (12), 55 (18).

Trimerization of cyclopentenone **24e** (**45b** *and* **46b**)

Cyclopentenone **24e** (1.0 g, 2.8 mmol) was converted to its trimers **45b** (0.26 g, 33%) and **46b** (0.14 g, 25%) with t-BuOK (0.5 g) as described above.

Compound **45b**. TLC (benzene–EtOAc 3:1) R_f = 0.55. IR (film): 1740, 1705 (CO), 1630 (C=C), 1460, 1410, 1380, 1350, 1290, 1180, 1070, 880 cm^{-1}. MS: M^+ 876 (< 1), *m/e* 660 (78), 604 (17), 444 (61), 364 (44), 159 (54), 143 (70), 103 (100), 87 (59), 61 (63), 57 (95).

Compound **46b**. TLC (benzene–EtOAc 3:1) R_f = 0.42. IR (film): 1740, 1705 (CO), 1620 (C=C), 1460, 1410, 1380, 1350, 1290, 1090, 1070, 1040, 880 cm^{-1}. MS: M^+ 660 (16), *m/e* 603 (64), 444 (13), 173 (58), 159 (59), 117 (66), 103 (100), 75 (32), 61 (82).

Methyl 7-(2,5-*dioxo*-1-*cyclopentyl*)-5(Z)-*heptenoate* (**13**)

Methoxycyclopentenone **11b** (0.25 g, 1 mmol) was hydrolysed in a mixture of MeOH–H_2O–HCl (2:1:0.1, 3 ml) at room temp (3 hr). Usual work-up followed by chromatography gave **13** (0.15 g, 63%).[17]

Methyl 7-(2,4-*dioxo*-1-*cyclopentenyl*)-5(Z)-*heptenoate* (**12**)

Methoxycyclopentenone **9b** was hydrolysed as described above to afford **12** in 62% yield (a mixture of keto and enol forms). Found: C, 65.38; H, 7.42. $C_{13}H_{18}O_4$, requires: C, 65.57; H, 7.56%. IR (film): 3300 (OH), 1725, 1700 (CO), 1610 (C=C), 1460, 1440, 1360, 1235, 1160, 1130, 1080, 1015 cm^{-1}. ^{1}H-NMR (CCl_4): δ 1.7 (2H, m, CH_2, C_2), 1.95–2.6 (9H, m, $4CH_2$, CH), 3.2 (1H, m, exchangeable with D_2O, OH), 3.55 (3H, s, OCH_3), 5.35 (3H, m, CH=CH, =CH). MS: M^+ 238 (12), *m/e* 206 (8), 178 (5), 164 (8), 149 (12), 122 (11), 110 (20), 90 (18), 76 (35), 58 (38), 54 (72), 49 (100).

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Compound **7b** was previously obtained as a side product of the cleavage of the isopropylidene derivative of 2[6-methoxycarbonyl-2(*Z*)-hexenyl - 3,4 - dihydroxycyclopentanone; L. Gruber, I. Tömösközi, E. Major and G. Kovács, *Tetrahedron Lett.* 3729 (1974). Recently, we have repeated this preparation and found the product to be a 3 : 2 mixture of *R*- and *S*-enantiomers.

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