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SYNTHESIS OF CYCLOPENTADIENONE EPOXIDES FROM 10-OXATRICYCLODECADIENONES[1].

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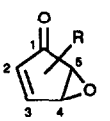
Abstract: Various 10-oxatricyclodecadienone epoxides have been prepared in high yields by a stereospecific nucleophilic epoxidation of the corresponding 10-oxatricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-ones. These polycyclic epoxides could efficiently be converted into cyclopentadienone epoxides using Flash Vacuum Thermolysis. The synthetic potential of the last named epoxides in the field of natural product synthesis is illustrated by the preparation of an epi-*pentenomycin.*

Introduction

The unique combination of an epoxide ring, a vinyl system and a carbonyl group within a compact, small ring system makes the cyclopentadienone epoxides **1** a fascinating class of compounds. Mutual interaction of these functional groups will be inevitable and special chemical behaviour may thus be expected. As these functionalities and their combinations all are susceptible for both nucleophilic and electrophilic attack, a well defined choice of reagents and reaction conditions will presumably be necessary to attain chemo- and regioselectivity.



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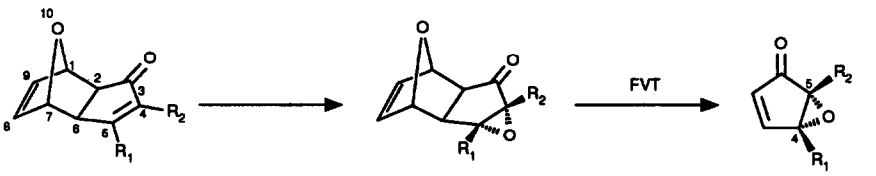
In the literature so far only a few members of this class of compounds have been described. Especially their photochemistry has been studied in detail. Tri- and tetraphenyl substituted cyclopentadienone epoxides have been observed to equilibrate with pyrylium oxides on irradiation[3,4]. Photochemically induced rearrangements to 2-pyrones have been reported for the parent compound **1** (R=H)[5] and for the alkyl- and phenylsubstituted compounds **1** (R=2,5-dimethyl; R=3,4-diphenyl; R=2,3,4,5-tetraphenyl)[6-9]. The frequently postulated intermediacy of cyclopentadienone epoxides in the photo-isomerisation of 4-pyrones to 2-pyrones has unambiguously been established for **1** (R=2,5-dimethyl)[6]. Moreover, phenyl-, alkyl- and otherwise substituted cyclopentadienone epoxides have been found to rearrange to 2-pyrones on heating[3,5,10-12]. The parent compound **1** (R=H) has been reported to decompose in acidic or basic media[5]. Only a few reports mention a synthetic application of these epoxides[2,13,14].

It is clear that a systematic study of cyclopentadienone epoxides was hampered by the difficult accessibility of these substrates. A general entrée to these compounds not only would allow a systematic study of their chemical behaviour but would also have a considerable synthetic impact, as these epoxides are potentially valuable synthons for the preparation of highly oxygenated cyclopentenoid natural products. Their apparent chemical sensitivity presumably will prevent a general preparation using normal chemical procedures. But, thanks to the development of advanced thermolysis techniques[15] neutral synthetic methods are now available, which can be applied in preparing epoxides of type **1**.

In the preceding paper[16] we presented our strategy towards cyclopentenones via Flash Vacuum Thermolysis (FVT) of appropriately functionalized tricyclic precursors. We selected 10-oxatricyclodecadienones **2** as potential synthons for the FVT mediated synthesis of substituted cyclopentadienone epoxides and described *in extenso* the preparation of such tricyclic enones from the Diels Alder adduct of furan and cyclopentene-1,4-dione.

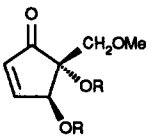
In the present report we focus on the utilisation of these oxatricyclodecadienones for the synthesis of 4- and/or 5-substituted cyclopentadienone epoxides **4**, according to the pathway indicated in Scheme 1.

Scheme 1



2 **3** **4**

To illustrate the synthetic potential of such epoxides in the field of natural product synthesis, we here also describe the selective cleavage of the epoxide ring of **4** (R_1=H; R_2=CH_2OMe) leading to the *epi*-pentenomycin analogues **5a,b**.



5a R=H

5b R=Ac

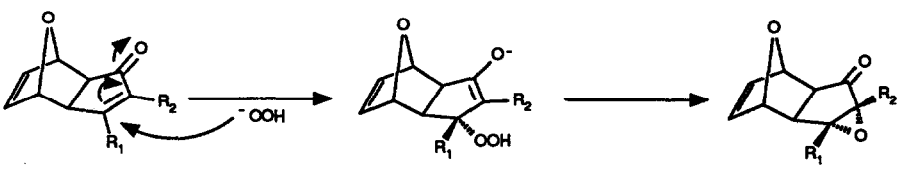
Results and Discussion

Alkaline epoxidation of 10-oxatricyclodecadienones **2**.

The ultimate conversion of the tricyclic enones **2** into the epoxides **4** involves two transformations (Scheme 1). The first one is a regioselective epoxidation of the electron poor double bond between C-4 and C-5 of the substrates **2**, to afford the corresponding epoxy ketones **3**. This epoxidation was carried out with alkaline

hydrogen peroxide, which is the common reagent for such a nucleophilic epoxidation (Scheme 2). Yields were

Scheme 2



generally close to quantitative, see Table 1. Some attention had to be payed to the amount of hydrogen peroxide in the epoxidation of the thioethers **2e** and **2f**. Too great an excess presumably also brings about some oxidation on sulphur, as is suggested by the lower yields obtained for **3e** and **3f**.

Table 1

substr. no.	R_1	R_2	product no.	yield[a] [%]
2a	H	H	**3a**	94
2b	H	CH_2OMe	**3b**	98
2c	H	CH_2OEt	**3c**	95
2d	H	CH_2OiPr	**3d**	94
2e	H	CH_2SPh	**3e**	60[b]
2f	H	CH_2SBz	**3f**	77[b]
2g	Me	H	**3g**	93
2h	Me	CH_2OMe	**3h**	100

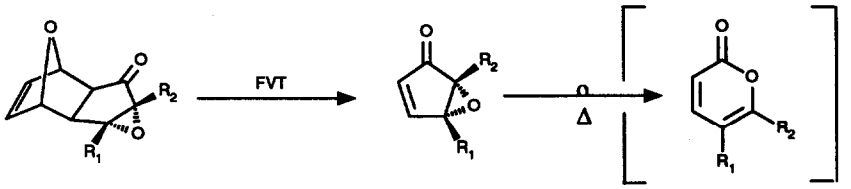
a. Except for **3e** and **3f** the yields given refer to crude products (purity *ca.* 95%).
b. Yield after flash chromatography.

The alkaline epoxidation turned out to be a stereospecific process. In all cases only one diastereomer was formed as was indicated by melting points, ^{1}H-NMR and capillary GC data. In conformity with the stereochemistry postulated[2,5,17-19] and found[16,20] for such tricyclic enones, the peroxide anion is expected to enter stereospecifically from the least hindered side of the molecule, *anti* to the oxa-bridge, adding in a conjugate fashion to the enone moiety of **2** (Scheme 2). In the products **3** the epoxide ring will thus be orientated as indicated in Scheme 2. To remove any doubts about this mechanism and about the final structure of the products, epoxide **3b** was subjected to an X-Ray analysis. This structure determination indeed confirmed the anticipated *exo*-configuration of the epoxide ring[21]. It is most likely that for the oxatricyclodecadienones **2** the steric bulk and the electronegative nature of the oxa-bridge cooperate in the steric approach control of incoming nucleophiles.

Flash vacuum thermolysis of the 10-oxatricyclodecadienone epoxides **3**.

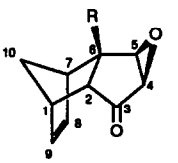
The second step in the route to cyclopentadienone epoxides **4** is a retro Diels-Alder reaction of the furan adducts **3** (Scheme 1). In view of the aromatic nature of furan, moderate cycloreversion temperatures were anticipated. We hoped that at these temperatures the thermally induced rearrangement of the epoxides **4** to the corresponding 2-pyrones **6** would not take place (Scheme 3).

Scheme 3



3 **4** **6**

Thermal cycloreversions can be accomplished under various conditions. We chose to employ the FVT technique since in previous work[12,13,17] excellent results had been obtained for the FVT cycloreversions of the 10-carbon analogues **7**. It should be noted however, that other techniques may be applied as well to accomplish



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the thermal cycloreversion of the 10-oxatricyclodecadienone epoxides **3**. This is demonstrated by Oda et al[22] who performed the thermolysis of **3a** to afford **4a** by sublimation under reduced pressure (300 mm Hg) in a short path distillation apparatus at 120~140°C. In our FVT set-up[23] (quartz pyrolysis tube (16x1.3 cm), P~10^{-2} mbar) the thermal conversion of **3a** was brought about at 375°C and 0.05 mbar, affording the parent cyclopentadienone epoxide **4a** in 90% yield as the sole product (see Table 2, entry 1). Lower temperatures resulted in incomplete or no conversion, while higher temperatures soon led to substantial amounts of pyrone **6a**. Already at 425°C a 1:1 mixture of **4a** and **6a** was obtained in 90% total yield (compare entry 1 and 1*, respectively). The thermolyses of the 4-substituted tricyclodecadienone epoxides **3b-f** were carried out using the same equipment. To avoid undesired pyrone formation small adjustments in temperature and pressure had to be made, but, having established those optimum conditions, the epoxides **4b,c,e,f** were obtained in virtually quantitative yields (entry 2,3,5,6). For **3d** the reaction conditions were not optimized. We expect however, that a thermolysis temperature between 300° and 340°C will give **4d** as the only product (compare entries 2,3,5 and 6). With the equipment indicated, the pyrone formation could not be avoided during the syntheses of the 4-substituted epoxides **4g** and **4h** from **3g** and **3h**, respectively. To minimize the pyrone production, a longer pyrolysis tube (25x1.3 cm) and oven were chosen, while the vacuum was kept at the same level. The longer contact time resulting therefrom

allowed a lower thermolysis temperature, however, not low enough to avoid the pyrone formation completely. The conditions affording optimum yields for **4g** and **4h** are included in Table 2, *viz.* entry 7 and 8, respectively. The high yields obtained in the above thermolyses demonstrate that furan derived adducts, such as **2**, are excellent precursors for an FVT mediated synthesis of cyclopentadienone epoxides.

In the thermolysates obtained from **3g**, two pyrones, *viz.* 5-methyl-2-pyrone (**6g**) and 3-methyl-2-pyrone (**6g***), were found instead of the single pyrone observed in the other thermolyses. The formation of all these pyrones **6a-h** from the corresponding cyclopentadienone epoxides **4a-h** is explained in Scheme 5.

Table 2

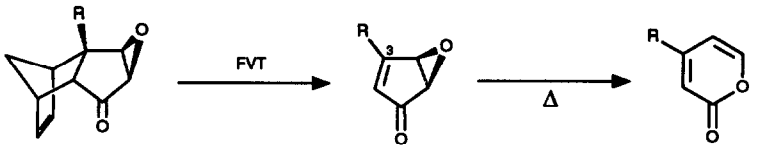
		thermolysis conditions		composition of the pyrolysate[b]					
	substr.	P	T_2/T_1[c]	products				substr.	
entry[a]	no.	[mbar]	[°C]	no.	[%]	no.	[%]	no.	[%]
1.	**3a**	0.05	375/75	**4a**	90	**6a**	-	**3a**	<5
1*.		0.06	425/75		45		45		-
2.	**3b**	0.06-0.08	360/90	**4b**	90	**6b**	<5	**3b**	<5
3.	**3c**	0.05	340/90	**4c**	≥90	**6c**	<5	**3c**	-
3*.		0.06	525/110				84		-
4.	**3d**	0.05-0.06	350/70[d]	**4d**	75[d]	**6d**	25[d]	**3d**	-
5.	**3e**	0.2	300/135	**4e**	95	**6e**	-	**3e**	-
6.	**3f**	0.2	300/135	**4f**	95	**6f**	-	**3f**	-
7.	**3g**	0.09-0.15	355/65	**4g**	85	**6g/6g***	15	**3g**	-
8.	**3h**	0.08-0.09	310/70	**4h**	84	**6h**	11	**3h**	<5

a. The thermolyses 1-6 were carried out in a short oven (16 x 1.3 cm); for the thermolyses 7 and 8 a longer oven (25 x 1.3 cm) was used.
b. The compositions of the pyrolysates were calculated from their ^{1}H-NMR spectra.
c. T_1= preheating temp; T_2= thermolysis temp.
d. Conditions not optimized, see text.

The 10-oxatricyclodecadienone epoxides **3** were found, as expected to undergo the [4+2] cycloreversion at considerably lower temperatures than their carbon analogues **7**. Whereas the flash vacuum thermolyses of the former led to complete conversion at temperatures ranging from 300-375°C, the thermolyses of the latter required generally temperatures up to or even higher than 500°C. Only in those cases, in which the resulting cyclopentadienone epoxide possessed a π-substituent at C-3, the temperature needed for the cycloreversion was lower, *viz. ca* 430°C (Scheme 4)[12,13]. Such a π-substituent enhances the thermodynamic stability of the products **8** by extending the conjugation of the enone moiety and as a result thereof the E_{act} of the cycloreversion is appreciably lowered. The E_{act} of the thermal rearrangement to 2-pyrones, however, is increased by this same stabilisation. This increase is apparently sufficiently large to allow the isolation of the cyclopentadienones **8**, even when relatively high thermolysis temperatures are applied. In the absence of such a π-substituent the temperatures of these cycloreversions are too high (≥ 500°C) to allow the isolation or even detection of the cyclopentadienone epoxides. Then only 2-pyrones are obtained[17].

An additional and significant factor influencing the temperature of the cycloreversion is the relative steric energy of the polycyclic epoxides **3**. The data collected in Table 2 suggest that an increase in size of the substituent at C-4 considerably facilitates the cycloreversion process. This is particularly striking for the thioethers **3e** and **3f** for which the optimum FVT temperatures are about 50°C lower than for the ethers **3b-d**.

Scheme 4



7a R: COOEt **8a** **9a**
7b R: CHO **8b** **9b**
7c R: CH=CHMe **8c**

Since the C-4 substituent is positioned *syn* with respect to the 10-oxa-bridge, this observation may be rationalized by assuming a considerable enhancement in the steric energy of **3** as a result of an increased interaction with the 10-oxa-bridge. The fact that this change in steric energy is apparently large enough to facilitate the cycloreversion process is another demonstration of the proximity effect of the 10-oxa-bridge in tricyclic structures such as **2** and **3**.

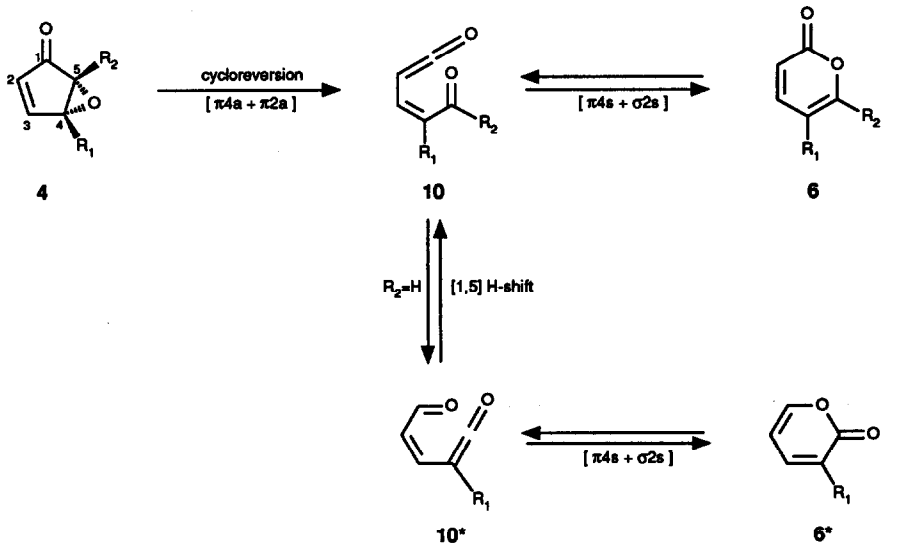
The influence of a substituent at C-5 was not studied in detail. Such a substituent will experience a smaller steric influence from the 10-oxa-bridge than a substituent at C-4 and will therefore presumably hardly reduce the temperature of the cycloreversion.

The epoxides **4a-h** appeared much easier to handle than anticipated from the literature.[4-7] They could be stored in the freezer without noticeable deterioration and were not affected during purification using flash chromatography. During their isolation their relatively high volatility had to be taken into account.

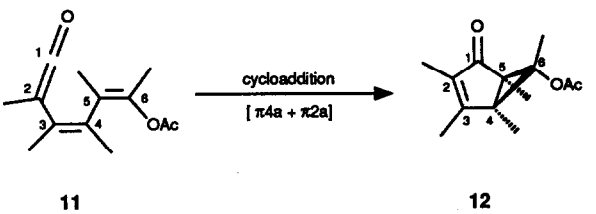
Their spectral features are characteristic for their structure. The IR absorption for the carbonyl group appears at 1732 cm^{-1}. In the ^{1}H-NMR spectra a typical[24] set of (double) doublets is found for the olefinic protons, H_3 and H_2, at δ 7.5 ± 0.1 and δ 6.0 ± 0.1 ppm, respectively. The signal for H_4 (m or d) appears at δ 4.0 ± 0.2 ppm and the (double) doublet for H_5 at δ 3.6 ± 0.1 ppm. These ^{1}H-NMR data are in agreement with the reported[5] resonances of the parent compound **4a**. The relatively low field position of H_4, as compared with H_5, is remarkable. The electron density at C-4 is apparently lower than at C-5. It shows that the electronegative influence of the carbonyl group efficiently is transferred by the C-2, C-3 double bond.

The thermally induced rearrangement of cyclopentadienone epoxides to 2-pyrones has previously been discussed and is suggested to proceed by a sequence of thermal pericyclic reactions, as presented in Scheme 5[12]. This mechanism is supported by the observation of Pirkle and Turner[25] that ketene aldehydes **10** (R_2=H) at elevated temperatures reversibly close to 2-pyrones or undergo reversible [1,5] sigmatropic H-shifts (Scheme 5). The occurrence of such 1,5-shifts explains the concomitant formation of pyron **6g*** in the thermal rearrangement of epoxide **4g** to pyron **6g**. Furthermore, the initial [π4a + π2a] cycloreversion reaction to ketene aldehyde **10** is in fact related to the conversion of ketene **11** into the bicyclic compound **12** (Scheme 6), for which transformation a similar [π4a + π2a] pericyclic pathway has been posited by Morris and Waring[26].

Scheme 5



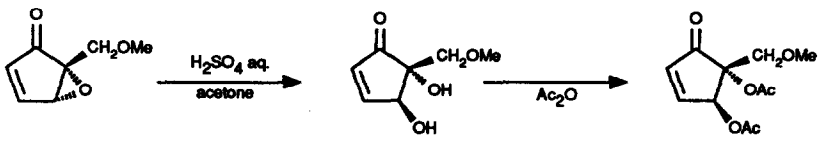
Scheme 6



Selective opening of the epoxide ring of **4b**. *Synthesis of* epi-*pentenomycin analogues*, **5a** *and* **5b**.

As indicated in the introduction, subtle conditions are probably necessary to achieve a selective reaction with the epoxide function in cyclopentadienone epoxides. Previous work[13] on **8c** (*vide supra*) had revealed that the epoxide group of this particular substrate is significantly less sensitive to acid hydrolysis than anticipated. Its epoxide ring was not affected by treatment with 0.4 N H_2SO_4 in ether. However, in acetone containing 1% 5N H_2SO_4 a selective opening leading to a trans diol was accomplished. Application of the last mentioned acidic conditions to **4b** led to a smooth cleavage of the epoxide ring, affording the methyl protected *epi*-pentenomycin, **5a** (Scheme 7)[27].Comparison of the ^{1}H-NMR spectra of the resulting diol **5a** and its acylated derivative **5b**, with the spectra of their epimers[17], confirmed unambiguously the *trans*-configuration of the diol group. The overall yield of this conversion appeared to vary between 30% and 55%. Presumably, both the high solubility of diol **5a** in water and the reactive nature of **4b** and **5a** disfavour a high and reproducible yield.

Scheme 7



4b 5a 5b

Concluding remarks

The results presented in this paper demonstrate that the 10-oxatricyclodecadienones **2** offer a general and stereospecific route to 4- and/or 5-substituted cyclopentadienone epoxides **4**. In most cases the competing formation of 2-pyrones can almost completely be suppressed by an appropriate choice of the FVT conditions. The versatility of the cyclopentadienone epoxides **4** for the synthesis of cyclopentenoid natural products is demonstrated by the synthesis of the *epi*-pentenomycin analogues **5a** and **5b**. Further exploration of the chemistry of cyclopentadienone epoxides will be dealt with in forthcoming papers.

Experimental

General remarks

Melting points were measured with a Reichert Thermopan microscope and are uncorrected. IR spectra were taken on a Perkin Elmer 298 infrared spectrophotometer. ^{1}H-NMR spectra were recorded on a Varian EM-390 or a Bruker WH-90 spectrometer using TMS as internal standard. For mass spectra a Varian SM-1B or a double focussing VG 7070E mass spectrometer was used. Column chromatography under light pressure ("flash chromatography"[28]) was carried out at a pressure of *ca* 1.5 bar, a column length of *ca* 15 cm and a column diameter of 1-4 cm, using Merck Kieselgel 60 H or Merck Aluminium Oxid 150 neutral (Typ T).

Oxa-tricyclodecadienone epoxides **3a-h** *via alkaline epoxidation of oxatricyclodecadienones* **2a-h**: *general procedure*[29].

To a 0.5-0.1 M solution of **2a-h**[16] in a 1:1 mixture of methanol and dichloromethane were successively added, 35% hydrogen peroxide (2-3 eq) and 0.2 N sodium hydroxide (0.04-0.06 eq). The mixture was stirred vigorously for *ca.* 3 hrs and then diluted with dichloromethane and water (CH_2Cl_2:H_2O = 2:1). The aqueous phase was extracted with dichloromethane (3x). The combined organic solutions were washed with water (3x), dried ($MgSO_4$), filtered and evaporated. The crude epoxides were generally sufficiently pure (^{1}H-NMR and capillary GC data) for further use. Analytically pure samples were obtained by crystallization or flash chromatography.

Exo-*4,5-epoxy*-exo-*10-oxatricyclo[5.2.1.0^{2,6}] deca-8-en-3-one* (**3a**).

The epoxidation of **2a**[16] (1.4 g; 9.1 mmol) was carried out as described in the general procedure, yielding 1.47 g (94%) of **3a**. The capillary GC diagram of the crude product showed 3 peaks, belonging to

epoxy-cyclopentenone **4a** (6.1%), pyrone **6a** (3.3%) and epoxide **3a** (90%), respectively. The first two compounds are not impurities, but result from thermolysis of **3a** in the injection port of the capillary GC. The ^{1}H-NMR soectrum confirmed the purity (≥ 95%) of the crude sample. Crystallization from n-hexane afforded analytically pure **3a**, mp 87-88°C (white needles). IR(KBr) ν(s): 1730(br,C=O), 1372, 1325/1315, 1262, 1219/1210/1202, 1190, 1042, 1020/1012, 950/935/928, 910, 880, 860/850, 832, 810/802, 715/705, 610 cm^{-1}. ^{1}H-NMR($CDCl_3$) δ: 2.31(1H,dd,$J_{6,5}$=1.1Hz,$J_{6,2}$=5.9Hz;H_6), 2.69(1H,d,$J_{2,6}$=5.9Hz;H_2), 3.58(1H,dd, $J_{4,2}$=0.8Hz,$J_{4,5}$=2Hz;H_4), 3.86(1H,m,$J_{5,4}$=2Hz;H_5), 5.07(2H,s;H_1,H_7), 6.42(1H,dd,J=1.5 resp 6Hz)/6.55(1H,dd, J=1.5 resp 6Hz)(H_8,H_9). The signals for H_2, H_4, H_5 and H_6 were assigned after spin decoupling. MS(CI) m/e(%): 165(24;M+1$^+$), 147(9;-H_2O), 137(8;-CO), 125(14), 111(8), 97(49;-furan), 91(16), 81(7),69(60;furan+1$^+$), 68(100;furan$^+$). (Found: C 65.68, H 5.01. Calc. for $C_9H_8O_3$: C 65.85, H 4.91%.)

Exo-*4,5-epoxy*-endo-*4-methoxymethyl*-exo-*10-oxatricyclo[5.2.1.0^{2,6}]deca-8-en-3-one* (**3b**).

The epoxidation of **2b**[16] (780 mg; 4.0 mmol) was carried out as described in the general procedure, yielding 813 mg (98%) of **3b**. The ^{1}H-NMR spectrum of the crude product showed no contaminants. Flash chromatography (Al_2O_3/hexane-ethyl acetate (3:1)) afforded analytically pure **3b** as a thick white oil, which solidified in the freezer (capillary GC output: 3 peaks, epoxy-cyclopentenone **4b** (45%), pyrone **6b** (1%) and epoxide **3b** (52%), respectively). IR(CCl_4) ν(s): 1742(C=O), 1122, 1090(C-O), 1028, 870, 700 cm^{-1}. ^{1}H-NMR($CDCl_3$) δ: 2.35(1H,br d,$J_{6,2}$=5.8Hz;H_6), 2.57(1H,d,$J_{2,6}$=5.8Hz;H_2), 3.34(3H,s;OCH_3), 3.60/3.74/3.83/3.97(2H,AB_q,J_{AB}=12.6Hz;CH_2OMe), 3.92(1H,br s;H_5), 5.05(2H,br s;H_1,H_7), 6.41(dd,J=1.8 and 5.4Hz)/6.54(dd,J=1.8 and 5.4Hz)(2H;H_8,H_9). MS(CI) m/e(%)[30]: 209(1;M+1$^+$), 169(11), 141(17;-furan), 109(100; -furan,-CH_3OH), 95(25;M$^+$-furan,-CH_2OCH_3), 81(45;-furan,-CH_3OH,-CO), 68(23;furan$^+$), 45(19;$CH_2OCH_3^+$). HRMS(CI) m/e: 209.0803 (calc. for $C_{11}H_{13}O_4$(M+1): 209.0814).

Exo-*4,5-epoxy*-endo-*4-ethoxymethyl*-exo-*10-oxatricyclo[5.2.1.0^{2,6}]deca-8-en-3-one* (**3c**).

The epoxidation of **2c**[16] (206 mg; 1.0 mmol) was carried out as described in the general procedure, yielding 210 mg (95%) of **3c**. The ^{1}H-NMR spectrum of the crude product showed no contaminants. Flash chromatography (Al_2O_3/hexane-ethyl acetate(5:1)) afforded analytically pure **3c** as a colourless oil (capillary GC output: 2 peaks, epoxy-cyclopentenone **4c** (32%) and epoxide **3c** (68%)). IR(film) ν(s): 1732(C=O), 1115, 1090(C-O), 870, 703, 610 cm^{-1}.^{1}H-NMR($CDCl_3$) δ: 1.11(3H,t,J=6.5Hz;OCH_2CH_3), 2.32(1H,dd,$J_{6,5}$=1.1Hz, $J_{6,2}$=6Hz;H_6), 2.57(1H,d,$J_{2,6}$=6Hz;H_2), 3.49(2H,q,J=6.5Hz;OCH_2CH_3), 3.65/3.78/3.83/3.97(2H,AB_q,J_{AB}=13Hz; CH_2OEt), 3.89(1H,d,$J_{5,6}$=1.1Hz;H_5), 5.00(2H,br s;H_1,H_7), 6.35(1H,dd,J=1.5 and 5.8Hz)/6.48(1H,dd,J=1.5 and 5.8Hz)(H_8,H_9). The assignment of the signals for H_5 and H_6 was confirmed by spin decoupling.

Exo-*4,5-epoxy*-endo-*4-isopropoxymethyl*-exo-*10-oxatricyclo[5.2.1.0^{2,6}]deca-8-en-3-one* (**3d**).

The epoxidation of **2d**[16] (402 mg; 1.8 mmol) was carried out as described in the general procedure, yielding 400 mg (94%) of **3d**, as a thick, white oil. The ^{1}H-NMR spectrum of this product showed no contaminants. Crystallization from n-pentane failed. IR(film) ν(s): 2960/2920/2865(sat C-H), 1738(C=O), 1380/1370(i-Pr), 1150, 1125, 1090(C-O), 905, 870, 805, 703, 610 cm^{-1}. ^{1}H-NMR($CDCl_3$) δ: 1.05(6H,d,J=6Hz; $CH(CH_3)_2$), 2.33(1H,dd,$J_{6,5}$=1.3Hz,$J_{6,2}$=5.8Hz;H_6), 2.54(1H,d,$J_{2,6}$=5.8Hz;H_2), 3.75(1H,septet,J=6Hz;$CH(CH_3)_2$), 3.67/3.79/3.82/3.96(2H,AB_q,J_{AB}=12.5Hz;CH_2OiPr), 3.89(1H,d,$J_{5,6}$=1.3Hz;H_5), 4.74(2H,br s;H_1,H_7), 6.31(1H, dd,J=1.5 and 5.6Hz)/6.44(1H,dd,J=1.5 and 5.6Hz)(H_8,H_9). MS(CI) m/e(%)[30]: 237(30;M+1$^+$), 177(24;-C_3H_7OH), 169(100;-furan),

145(38),127(79;-furan,-C_3H_6), 110(22;-furan,-OC_3H_7), 109(22;-furan,-C_3H_7OH), 95(16;M^+-furan, -CH_2OiPr), 81(20;-furan,-C_3H_7OH,-CO), 68(13;furan$^+$). HRMS(CI) m/e: 237.1123 (calc. for $C_{13}H_{17}O_4$(M+1): 237.1127).

Exo-*4,5-epoxy*-endo-*4-phenylthiomethyl*-exo-*10-oxatricyclo[5.2.1.0^{2,6}]deca-8-en-3-one* (**3e**).

The epoxidation of **2e**[16] (115 mg; 0.43 mmol) was carried out as described in the general procedure, yielding 100 mg (*ca.* 82%) of crude **3e**. Purification by flash chromatography (Al_2O_3/hexane-ethyl acetate (5:1)) left 73 mg (60%) of pure product. IR(KBr) v: 1738(s), 1700(m), 1470(m), 1440(m), 1408(m), 1198(m), 1143(m), 1098(m), 1028(m), 1008(m), 920(m), 872(s), 802(m), 755(s), 695(s) cm^{-1}. ^{1}H-NMR($CDCl_3$) δ: 2.40(1H,dd, $J_{6,7}$=0.8Hz,$J_{6,2}$=6.1Hz;H_6), 2.52(1H,d,$J_{2,6}$=6.1Hz;H_2), 3.13/3.30/3.50/3.67(3H,AB_q+ s,J_{AB}=15.2Hz;CH_2SPh + H_5 (3.67 ppm)), 4.80(1H,d,$J_{7,6}$=0.8Hz;H_7), 5.10(1H,br s;H_1), 6.38(1H,dd,J=1.4 and 5.6Hz)/6.51(1H,dd,J=1.4 and 5.6Hz)(H_8,H_9), 7.28(5H,m;ArH). MS(EI) m/e(%)[30]: 286(27;M^+), 218(51;-furan), 123(2;CH_2SPh^+), 109(88; -furan,-SPh and/or SPh^+), 95(100;-furan,-CH_2SPh), 77(23;$C_6H_5^+$), 68 (16;furan$^+$). (Found: C 66.80, H 4.87. Calc. for $C_{16}H_{14}O_3S$: C 67.11, H 4.93%.)

Endo-*4-benzylthiomethyl*-exo-*4,5-epoxy*-exo-*10-oxatricyclo[5.2.1.0^{2,6}]deca-8-en-3-one* (**3f**).

The epoxidation of **2f**[16] (354 mg; 1.3 mmol) was carried out as described in the general procedure, yielding 353 mg (*ca.* 94%) of crude **3f**. Purification by flash chromatography (SiO_2/ethyl acetate), afforded 287 mg (77%) of pure **3f** as a colourless oil. IR(CCl_4) v: 1743(s), 1452(w), 1408(w), 1312(w), 1262(w), 1150(w), 1090(w), 1028(m), 910(m), 870(m), 700(s) cm^{-1}. ^{1}H-NMR($CDCl_3$) δ: 2.40(1H,dd,$J_{6,5}$=1.2Hz,$J_{6,2}$=6.0Hz;H_6), 2.57(1H,d,$J_{2,6}$=6.0Hz;H_2), 2.64/2.81/2.91/3.09(2H,AB_q,J_{AB}=15.4Hz;CH_2Ph), 3.73(2H,s;CH_2SBz), 3.84(1H,d, $J_{5,6}$=1.2Hz;H_5), 4.98(1H,d,J=1.4Hz)/5.08(1H,d,J=1.4Hz)(H_1,H_7), 6.40(1H,dd,J=1.4 and 5.6Hz)/ 6.53(1H,dd,J=1.4 and 5.6Hz)(H_8,H_9), 7.27(5H,br s;ArH). MS(CI) m/e(%): 301(6;M+1), 233(24;M+1-furan), 215(10;M+1-furan,-H_2O), 126(28), 110(10;M+1-furan,-SBz), 91(100;Bz^+), 69(15;(furan+1)$^+$). HRMS(CI) m/e: 301.0899 (calc. for $C_{17}H_{17}O_3S$ (M+1): 301.0898).

Exo-*4,5-epoxy*-endo-*5-methyl*-exo-*10-oxatricyclo[5.2.1.0^{2,6}]deca-8-en-3-one* (**3g**).

The epoxidation of **2g**[16] (725 mg; 2.4 mmol) was carried out as described in the general procedure, yielding 734 mg (93%) of **3g**, as a white solid. The ^{1}H-NMR spectrum of the crude product showed no contaminants. Crystallization from hexane-ethyl acetate (4:1) afforded analytically pure **3g**, mp 85-87°C. IR(KBr) v(s): 2940, 1750(C=O), 1400, 1255, 1232, 1192, 1110, 1075, 1022, 990, 852, 805, 715, 675, 615 cm^{-1}. ^{1}H-NMR($CDCl_3$/CCl_4) δ: 1.63(3H,s;CH_3), 2.27(1H,d,$J_{6,2}$=6Hz;H_6), 2.46(1H,d,$J_{2,6}$=6Hz;H_2), 3.30(1H,s;H_4), 4.98(br s)/5.04(br s)(2H;H_1,H_7), 6.44(2H,m;H_8,H_9). MS(EI) m/e(%): 178(0.7;M^+), 177(1.1;M-1), 149(1.5;M-1, -CO), 110(36;-furan), 82(48;-furan,-CO), 68(100;furan$^+$). (Found: C 67.49, H 5.66. Calc. for $C_{10}H_{10}O_3$: C 67.41, H 5.66%.)

Exo-*4,5-epoxy*-endo-*4-methoxymethyl*-endo-*5-methyl*-exo-*10-oxatricyclo[5.2.1.0^{2,6}]deca-8-en-3-one* (**3h**).

The epoxidation of **2h**[16] (676 mg; 3.3 mmol) was carried out as described in the general procedure, yielding 740 mg (100%) of **3h**, as a white solid. The ^{1}H-NMR spectrum of the crude product showed no contaminants. Crystallization from hexane-ethyl acetate (3:1) afforded analytically pure **3h**, mp 60-63°C. IR(KBr) v(s): 1735(C=O), 1120, 1015, 915, 870,720 cm^{-1}. ^{1}H-NMR($CDCl_3$) δ: 1.71(3H,s;CH_3), 2.38(1H, d,$J_{6,2}$=6.3Hz;H_6), 2.54(1H,d,$J_{2,6}$=6.3Hz;H_2), 3.37(3H,s;OCH_3), 3.56/3.69/3.89/4.02(2H,AB_q,J_{AB}=11.7Hz; CH_2OMe), 5.02(1H,br s)/5.10(1H,br s)(H_1,H_7), 6.46(2H,m;H_8,H_9). MS(CI) m/e(%)[30]: (no M^+, M+1 or M-1

peak), 205(11;M+1-H_2O), 155(33;M+1-furan), 123(100;M+1-furan,-CH_3OH), 109(17;M^+-furan,-CH_2OCH_3), 95(18; M+1-furan,-CH_2OCH_3,-CH_3), 68(furan$^+$). (Found: C 64.70, H 6.39. Calc. for $C_{12}H_{14}O_4$: C 64.85, H 6.35%.)

Flash-vacuum thermolysis of oxatricyclodecadienone epoxides, **3a-h**: *general remarks*.

The polycyclic epoxides **3a-h** were distilled or sublimed in vacuo through a hot quartz tube (16 or 25 x 1.3 cm). The pyrolysates were collected immediately after the pyrolysis tube in a cold trap at -78°C[23]. By carefully varying the pressure (P),the preheating temperature (T_1) and the oven temperature (T_2) optimum conditions were established for the majority of the reactions. Usually several runs were needed before the best conditions were found. The pyrolysates then often consisted of a mixture of unreacted substrate and products. The composition of these mixtures was at best deduced from ^{1}H-NMR data, as cap GC data sometimes gave a slightly distorted picture due to cycloreversion and rearrangement reactions taking place in the injection port of the capillary GC. The products could easily be isolated from the pyrolysates by flash chromatography on silicagel using a hexane-ethyl acetate mixture as the eluent. The isolation of the cyclopentadienone epoxides from the eluates required some care as these epoxides are rather volatile. In the experimentals below generally those conditions, that led to optimum yields of epoxides **4a-h** are given.

4,5-Epoxy-2-cyclopentenone (**4a**).

Flash vacuum thermolysis (16 cm tube/T_1 75°C/T_2 375°C/P 0.05 mbar/1.5 hr) of **3a** (164 mg; 1 mmol) provided 86 mg (*ca.* 90%) of **4a**. Only a small trace of **3a** (≤ 5%) was detected in the ^{1}H-NMR spectrum of the pyrolysate. Flash chromatography (SiO_2/hexane-ethyl acetate (3:1)) of crude product mixtures (see: *general remarks)* afforded pure **4a** as a colourless oil. IR(CCl_4)[5] ν: 1735(s;C=O), 1332(m), 1175(w)/1165(w), 1082(w)/1072(w), 993(w),960(w), 938(w), 845(s) cm^{-1}. ^{1}H-NMR($CDCl_3$)[5] δ: 3.67(dd;H_5), 4.14(m;H_4), 6.02(ddd;H_2), 7.63(dd;H_3).

Further eluation afforded successively **3a** and *2H-pyran-2-one* (**6a**) (colourless oil). IR(CCl_4)[5] ν: 1745(s;C=O), 1245(m), 1192(m), 1112(w), 1080(m), 1060(w) cm^{-1}. ^{1}H-NMR(CCl_4) δ: 6.05-6.17(1H,m;H_5), 6.17-6.33(1H,m;H_3), 7.13-7.39(1H,m;H_4), 7.39-7.42(1H,m;H_6).

The thermolysis of **3a** (61 mg; 0.4 mmol) at an oven temperature of 425°C (other conditions unchanged) led to a 1:1 mixture of epoxide **4a** and pyrone **6a** (32 mg; 90% total yield).

4,5-Epoxy-5-methoxymethyl-2-cyclopentenone (**4b**).

Flash vacuum thermolysis (16 cm tube/T_1 90°C/T_2 360°C/P 0.06-0.08 mbar/1.5 hr) of **3b** (99 mg; 0.5 mmol) provided 59 mg (*ca.* 90%) of **4b**. Only small traces (≤ 5%) of **3b** and pyrone **6b** were detected in the ^{1}H-NMR spectrum of the pyrolysate. Flash chromatography (SiO_2/hexane-ethyl acetate (3:2)) of crude product mixtures (see: *general remarks)* afforded pure **4b** as a colourless oil. IR(CCl_4) ν: 1732(s;C=O), 1332(m), 1198(w), 1135(m), 1103(m), 828(m) cm^{-1}. ^{1}H-NMR($CDCl_3$) δ: 3.40(3H,s;OCH_3), 3.73/3.87/3.99/4.16(2H,AB_q, J_{AB}=12Hz;CH_2OMe), 4.13(1H,br s;H_4), 6.00(1H,dd,$J_{2,4}$=2.2Hz,$J_{2,3}$=6Hz;H_2), 7.60(1H,dd,$J_{3,4}$=1.5Hz, $J_{3,2}$=6Hz;H_3). MS(EI) m/e(%): 140(2;M^+), 125(3;-CH_3), 110(5), 95(100;-CH_2OCH_3), 45(15;$CH_2OCH_3^+$). HRMS(EI) m/e: 140.0475 (calc. for $C_7H_8O_3$(M): 140.0473).

Further eluation afforded successively **3b** and *6-Methoxymethyl-2H-pyran-2-one* (**6b**) (colourless oil). IR(CCl_4) ν: 1745(s;C=O), 1640(w), 1560(m), 1200(w), 1125(m), 1090(m) cm^{-1}. ^{1}H-NMR(CCl_4) δ: 3.40(3H,

s;OCH_3), 4.15(2H,s;CH_2OMe), 6.02(1H,d,$J_{5,4}$=9.6Hz;H_5), 6.13(1H,d(d),$J_{3,4}$=6.2Hz,(J=1.3Hz);H_3), 7.18(1H,dd, $J_{4,3}$=6.2Hz,$J_{4,5}$=9.6Hz;H_4).

4,5-Epoxy-5-ethoxymethyl-2-cyclopentenone (**4c**).

Flash vacuum thermolysis (16 cm tube/T_1 90°C/T_2 340°C/P 0.05 mbar/4 hr) of **3c** (141 mg; 0.6 mmol) provided *ca.* 95 mg (≥ 90%) of **4c**. Only a small trace of pyrone **6c** (≤ 5%) was detected in the ^{1}H-NMR spectrum of the pyrolysate. Flash chromatography (SiO_2/hexane-ethyl acetate (3:2)) of crude product mixtures (see: *general remarks)* afforded pure **4c** as a colourless oil. ^{1}H-NMR($CDCl_3$) δ: 1.20(3H,tr,J=6.6Hz;$OCH_2\underline{CH_3}$), 3.54(2H,q,J=6.6Hz;$OC\underline{H_2}CH_3$), 3.75/3.89/4.05/4.18(2H,AB_q,J_{AB}=13Hz;CH_2OEt), 4.15(1H,m;H_4), 6.04(1H,dd, $J_{2,4}$=2.4Hz,$J_{2,3}$=6Hz;H_2), 7.60(1H,dd,$J_{3,4}$=1.5Hz,$J_{3,2}$=6Hz;H_3). MS(70eV) m/e: 154(M^+), 125(-C_2H_5), 109(-OC_2H_5), 95(-CH_2OEt), 59(CH_2OEt^+). HRMS m/e: 154.063 (calc. for $C_8H_{10}O_3$(M): 154.066).

Further eluation afforded successively **3c** and *6-Ethoxymethyl-2H-pyran-2-one* (**6c**) (colourless oil). IR(CCl_4) ν: 2978(m), 2920(m), 2860(m), 1740(s;C=O), 1640(m), 1560(m), 1315(m), 1195(,m), 1175(m), 1122(s), 1088(s) cm^{-1}. ^{1}H-NMR($CDCl_3$) δ: 1.24(3H,tr,J=7Hz;$OCH_2\underline{CH_3}$), 3.58(2H,q,J=7Hz;$OC\underline{H_2}CH_3$), 4.23(2H,br s;CH_2OEt), 6.21(1H,d,$J_{5,4}$=10Hz;H_5), 6.25(1H,d(d),$J_{3,4}$=6Hz,(J=1.2Hz);H_3), 7.29(1H,dd,$J_{4,3}$=6Hz, $J_{4,5}$=10Hz;H_4).

The thermolysis of **3c**, preheated at 110°C, at an oven temperature of 525°C and a pressure of 0.06 mbar led to pyrone **6c** as the only product in 84% yield.

4,5-Epoxy-5-iso-propoxymethylcyclopentenone (**4d**).

Flash vacuum thermolysis (16 cm tube/T_1 70°C/T_2 350°C/P 0.05-0.06 mbar/3 hr) of **3d** (223 mg; 0.9 mmol) produced a 3:1 mixture of epoxide **4d** and pyrone **6d** (131 mg; 87% total yield). Optimization of thermolysis conditions was not carried out. Flash chromatography (SiO_2/hexane-ethyl acetate (3:1)) of the pyrolysate afforded pure **4d** as a colourless oil (75%). IR(film) ν: 3070(w), 2968(s), 2922(m), 2868(m), 1722(s;C=O), 1380(m), 1368(m), 1335(s), 1178(m), 1125(s), 1080(s), 840(s), 825(s) cm^{-1}. ^{1}H-NMR(CCl_4) δ: 1.14(6H,d,J=6.7Hz;$CH(C\underline{H_3})_2$), 3.57(1H,septet,J=6.7Hz;$C\underline{H}(CH_3)_2$), 3.57/3.70/4.00/4.13(2H,AB_q,J_{AB}=11.4Hz; CH_2OiPr), 4.00(1H,br s;H_4), 5.97(1H,dd,$J_{2,4}$=1.9Hz,$J_{2,3}$=6Hz;H_2), 7.53(1H,dd,$J_{3,4}$=1.5Hz,$J_{3,2}$=6Hz;H_3). MS(CI) m/e(%): 169(59;M+1$^+$), 127(100;-C_3H_6), 109(34;-C_3H_7OH), 95(31;M^+-CH_2OiPr), 81(68;-C_3H_7OH,-CO), 73(5;CH_2OiPr^+), 43(12;$C_3H_6^+$). HRMS(CI) m/e: 169.0873 (calc. for $C_9H_{13}O_3$(M+1): 169.0865).

Further eluation afforded *6-iso-Propoxymethyl-2H-pyran-2-one* (**6d**) as a pale tinted oil. ^{1}H-NMR(CCl_4) δ: 1.17(6H,d,J=6.8Hz;$CH(C\underline{H_3})_2$), 3.63(1H,septet,J=6.8Hz;$C\underline{H}(CH_3)_2$), 4.17(2H,br s;CH_2OiPr), 6.01(1H,d, $J_{5,4}$=9.6Hz;H_5), 6.11(1H,d,$J_{3,4}$=7.1Hz;H_3), 7.17(1H,dd,$J_{4,3}$=7.1Hz,$J_{4,5}$=9.6Hz;H_4).

4,5-Epoxy-5-phenylthiomethyl-2-cyclopentenone (**4e**).

Flash vacuum thermolysis (16 cm tube/T_1 135°C/T_2 300°C/P 0.2 mbar/5 hr) of **3e** (95 mg; 0.33 mmol) provided 69 mg (95%) of epoxide **4e** as the only product. This epoxide was obtained as an oil. IR(CCl_4) ν: 3070/3050(w), 2955(w), 2923(w), 1736(s;C=O), 1480(w), 1438(w), 1332(w), 692(m) cm^{-1}. ^{1}H-NMR($CDCl_3$) δ: 3.22/3.38/3.61/3.77(2H,AB_q,J_{AB}=14.4Hz;CH_2SPh), 3.83(1H,dd,$J_{4,3}$=1.6Hz,$J_{4,2}$=2.0Hz;H_4), 6.07(1H,dd, $J_{2,4}$=2.0Hz,$J_{2,3}$=6Hz;H_2), 7.34(5H,m;ArH), 7.45(1H,dd,$J_{3,4}$=1.6Hz,$J_{3,2}$=6Hz;H_3). MS(EI) m/e(%): 218(57;M^+), 123 (16;CH_2SPh^+), 109(68;-SPh and/or SPh^+), 95(100;-CH_2SPh), 81(10), 77(10;$C_6H_5^+$), 65(15), 45(22), 39(31). HRMS(EI) m/e: 218.0391 (calc. for $C_{12}H_{10}O_2S$ (M): 218.0402).

5-Benzylthiomethyl-4,5-epoxycyclopentenone (**4f**).

Flash vacuum thermolysis (16 cm tube/T_1 135°C/T_2 300°C/P 0.2 mbar/6.5 hr) of **3f** (102 mg; 0.34 mmol) provided 75 mg (95%) of epoxide **4f** as the only product. This epoxide was obtained as an oil. IR(CCl_4) ν: 3060(w), 3025(w), 2918(w), 1734(s;C=O), 1452(m), 1408(m), 1333(m), 1028(m), 910(m), 700(s) cm^{-1}. ^{1}H-NMR($CDCl_3$) δ: 2.74/2.91/3.06/3.22(2H,AB_q,J_{AB}=15Hz;SCH_2Ph), 3.75(2H,br s;CH_2SBz), 3.90(1H,dd, $J_{4,3}$=1.4Hz,$J_{4,2}$=2.2Hz;H_4), 5.99(1H,dd,$J_{2,4}$=2.2Hz,$J_{2,3}$=6Hz;H_2), 7.26(5H,br s;ArH), 7.47(1H,dd,$J_{3,4}$=1.4Hz, $J_{3,2}$=6Hz;H_3). MS(EI) m/e(%): 232(2;M^+), 141(5;-$CH_2C_6H_5$), 126(54), 123(21;$SCH_2C_6H_5^+$), 122(13), 110(27), 95(27;-$CH_2SCH_2C_6H_5$), 91(100;$CH_2C_6H_5^+$), 82(12), 65(20), 45(17), 39(39). HRMS(EI) m/e: 232.0565 (calc. for $C_{13}H_{12}O_2S$ (M+1): 232.0558).

4,5-Epoxy-4-methyl-2-cyclopentenone (**4g**).

Flash vacuum thermolysis (25 cm tube/T_1 65°C/T_2 355°C/P 0.09-0.15 mbar/2 hr) of **3g** (320 mg; 1.8 mmol) provided 192 mg (97%) of a mixture of epoxide **4g** (85%), and pyrones **6g** and **6g*** (15%; *ca.* 2:3). Flash chromatography (SiO_2/hexane-ethyl acetate (4:1)) of crude product mixtures (see: *general remarks)* afforded pure **4g** as a colourless oil. IR(CCl_4) ν: 1745(s)/1722(s)(C=O), 1442(m), 1410(s), 1330(m), 1165(m), 1088(s), 1065(m), 900(s), 868(m), 700(m) cm^{-1}. ^{1}H-NMR($CDCl_3$) δ: 1.76(3H,s;CH_3), 3.54(1H,d,$J_{5,2}$=1.8Hz;H_5), 5.91(1H,dd,$J_{2,5}$=1.8Hz,$J_{2,3}$=6.1Hz;H_2), 7.46(1H,d,$J_{3,2}$=6.1Hz;H_3). MS(CI) m/e(%): 111(100;M+1$^+$), 85(17;-CO), 57(12). HRMS(CI) m/e: 111.0448 (calc. for $C_6H_7O_2$(M+1): 111.0446).

Further eluation afforded *3-Methyl-2H-pyran-2-one* (**6g***), ^{1}H-NMR(CCl_4)[25] δ: 2.00(3H,s;CH_3), 6.00(1H,tr,J=6Hz;H_5), 6.98(1H,d,$J_{4,5}$=6Hz;H_4), 7.32(1H,d,$J_{6,5}$=6Hz;H_6) and *5-Methyl-2H-pyran-2-one* (**6g**). IR(CCl_4) ν: 1748(s)/1725(m) (C=O), 1655(w)/1645(w), 1540(w), 1240(w), 1210(w), 1138(w), 1115(w) cm^{-1}. ^{1}H-NMR(CCl_4)[25] δ: 1.93(3H,s;CH_3), 6.16(1H,d,$J_{3,4}$=9.8Hz;H_3), 7.08(1H,dd,$J_{4,6}$<2Hz,$J_{4,3}$=9.8Hz;H_4), 7.20(1H,br s;H_6).

4,5-Epoxy-5-methoxymethyl-4-methyl-2-cyclopentenone (**4h**).

Flash vacuum thermolysis (25 cm tube/T_1 70°C/T_2 310°C/P 0.08-0.09 mbar/10 hr) of **3h** (161 mg; 0.72 mmol) provided 105 mg (*ca.* 95%) of a mixture of epoxide **4h** (84%) and pyrone **6h** (11%). Also a small trace (≤ 5%) of **3h** was detected in the ^{1}H-NMR spectrum of the pyrolysate. Flash chromatography (SiO_2/hexane-ethyl acetate (3:1)) of crude product mixtures (see: *general remarks)* afforded pure **3h** as a colourless oil. IR(CCl_4) ν: 2990(w), 2920(m), 2822(w), 1732(s;C=O), 1450(w), 1388(m), 1330(m), 1300(w), 1195/1190(m), 1132(m), 1108(s), 1088(m), 1043(m), 950(w), 902(w) cm^{-1}. ^{1}H-NMR($CDCl_3$) δ: 1.73(3H,s;CH_3), 3.40(3H,s;OCH_3), 3.61/3.73/4.04/4.18(2H,AB_q,J_{AB}=11Hz;CH_2OMe), 5.96(1H,d,$J_{2,3}$=6.3Hz;H_2), 7.44(1H,d,$J_{3,2}$=6.3Hz;H_3). MS(CI) m/e(%): 155(74;M+1$^+$), 123(100;-CH_3OH), 109(19;M^+-CH_2OCH_3), 95(70;-CH_2OCH_3,-CH_3), 45(15;$CH_2OCH_3^+$). HRMS(CI) m/e: 155.0710 (calc. for $C_8H_{11}O_3$(M+1): 155.0708).

Further eluation afforded *6-Methoxymethyl-5-methyl-2H-pyran-2-one* (**6h**). IR(CCl_4) ν: 2990(w), 2920(m), 2820(w), 1742(s;C=O), 1645(m), 1550(w), 1450(w), 1387(w), 1367(w), 1305(m), 1205(w), 1192(m), 1128(m), 1088(s), 1005(m), 862(m) cm^{-1}. ^{1}H-NMR(CCl_4) δ: 2.04(3H,s;CH_3), 3.38(3H,s;OCH_3), 4.16(2H,s; CH_2OMe), 6.18(1H,d,$J_{3,4}$=9Hz;H_3), 7.03(1H,d,$J_{4,3}$=9Hz;H_4). MS(CI) m/e(%): 155(100;M+1$^+$), 123(20;-CH_3OH), 109(4;M^+-CH_2OCH_3), 57(11), 45(10;$CH_2OCH_3^+$). HRMS(CI) m/e: 155.0706 (calc. for $C_8H_{11}O_3$(M+1): 155.0708).

(4R,5S*)-4,5-dihydroxy-5-methoxymethyl-2-cyclopentenone* (**5a**).

A solution of **4b** (86 mg; 0.6 mmol) in acetone (25 ml, containing 1% 5N H_2SO_4) was stirred for 2 days. Then $NaHCO_3$ (5 g) and $MgSO_4$ (5 g) were added and stirring was continued overnight. The solids were filtered off and carefully rinsed with acetone. The combined filtrates were concentrated to give 86 mg of crude **5a**, as a pale yellow oil. Purification of this material was not attempted. IR(film) ν: 3700-3040 (s;OH), 2980(m), 2920(m), 1710(s;C=O), 1635(s;C=C), 1100(s) cm^{-1}. ^{1}H-NMR(CD_3OD) δ: 3.33(3H,s;CH_2OCH_3), 3.57(2H,s; CH_2OCH_3), 4.73(1H,br s;H_4), 6.27(1H,br d,$J_{2,3}$=6Hz;H_2), 7.53(1H,dd,$J_{3,4}$=1.5Hz,$J_{3,2}$=6Hz;H_3).

Instead of purificaton, the crude diol **5a** was acylated by stirring it for 3 hrs in a solution of dichloromethane (4 ml) with Et_3N (0.3 ml), Ac_2O (0.2 ml) and DMAP (10 mg). After the usual work-up the crude product (151 mg, brown tinted oil) was purified by flash chromatography (SiO_2/ethyl acetate) to afford 78 mg of *(4R*,5S*)-4,5-diacetoxy-5-methoxymethyl-2-cyclopentenone* (**5b**), as a colourless oil (54% overall yield). IR(CCl_4) ν: 1735(broad s;C=O), 1370(m), 1245(s), 1220(s) cm^{-1}. ^{1}H-NMR($CDCl_3$) δ: 2.10(s)/2.13(s) (6H;2xCH_3), 3.33(3H,s;CH_2OCH_3), 3.55(2H,s;CH_2OCH_3), 6.26(1H,t,$J_{4,3}$=$J_{4,2}$=2Hz;H_4), 6.47(1H,dd,$J_{2,4}$=2Hz, $J_{2,3}$=6Hz;H_2), 7.40(1H,dd,$J_{3,4}$=2Hz,$J_{3,2}$=6Hz;H_3). MS(EI) m/e(%): 242 (0.71;M^+), 158(10;-2xCH_2CO), 140(51; -CH_2CO,-CH_3COOH), 113(19;-2xCH_2CO,-CH_2OMe), 95(63;-CH_2CO,-CH_3COOH,-CH_2OMe), 45(43;CH_2OMe^+), 43(100;CH_3CO^+). HRMS(EI) m/e: 242.0787 (calc. for $C_{11}H_{14}O_6$(M): 242.0790).

References and notes

1. Part of this work has already been published in a preliminary communication[2]. This paper provides a detailed and extended account.
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29. The procedure is based on the alkaline epoxidation of dicyclopentadiene-3-one, reported by Chapman and Hess[5].
30. The underscored signals are also found in the corresponding mass spectrum of the derived cyclopentadienone epoxide.