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A RING CONTRACTION OF 6-ALKOXY-2,3-DIHYDRO-6H-PYRAN-3-ONES TO POLYFUNCTIONALIZED CYCLOPENTENONES

Hartmuth C. Kolb* and H. Martin R. Hoffmann*

Department of Organic Chemistry
University of Hannover, Schneiderberg 1 B,
D-3000 Hannover, Federal Republic of Germany

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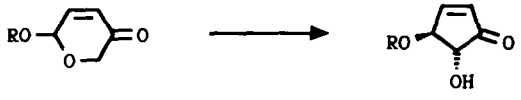
Abstract - The rearrangement of 6-alkoxy-2,3-dihydro-6*H*-pyran-3-ones (**1**) to *trans*-4-alkoxy-5-hydroxy-2-cyclopenten-1-ones (**2**) has been optimized. The effect of buffer concentration ($PhCO_2H$/KOAc) on reaction rate and yield suggests specific acid catalysis. Substitution patterns and influence of the 6-alkoxy substituent have been investigated. Applications in natural product synthesis are described.

A novel ring contraction of 6-alkoxy-2,3-dihydro-6*H*-pyran-3-ones (**1**) provides access to highly functionalized cyclopentenones **2**.[1]



1 **2**

We now report the optimization, investigations of scope and limitation and also mechanistic aspects of the rearrangement reaction.

Optimization. Initial experiments[1] under two phase conditions using $NaHCO_3$/$Pd(OAc)_2$ and $nBu_4N^+Cl^-$ gave varying results with respect to both reaction time and yield. Scale up of the reaction also proved problematic. We therefore probed the influence of phase transfer catalyst, solvent effects, acid/base catalysis and $Pd(OAc)_2$ on the rearrangement.

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*Current address: Department of Chemistry, Imperial College of Science, Technology and Medicine, London SW7 2AY, England.

Variation of PTC catalyst ($Et_3N^+CH_2PhCl^-$, $nBu_4N^+Cl^-$) in the presence of $NaHCO_3$ (5 eq) and $Pd(OAc)_2$ (2 mol%) showed no clear trends. Use of $nBu_4N^+HSO_4^-$ instead of $nBu_4N^+Cl^-$ led to exclusive decomposition of starting material.

A change of solvent from N,N-dimethylformamide (DMF) to acetonitrile caused a drop in yield (from 56% to 41%, cf. Table II, entry **b**). A decrease of solvent polarity (to toluene) entailed a further drop in yield and reaction rate.

Since no product was obtained when $NaHCO_3$ was substituted by K_2CO_3, we assumed that H^+ activity played an important role. In order to obtain reproducible results we chose homogeneous instead of PTC conditions. Potassium acetate and benzoic acid showed reasonable solubility in hot DMF. A variation of the buffer ratio HOBz : KOAc in the range of 1 : 1 to 0 : 2 suggested a bell-shaped dependence of yield on proton activity, the optimum ratio being 1 : 2 (Table I, entries 2, 5 and 6). Reaction times were generally shorter (ca 70 min) than those under heterogeneous conditions (ca 10 - 20 h).

The effect of added $Pd(OAc)_2$ was not discernible under these conditions (Table I, entries 1 and 2).

Table I. Influence of Buffer Ratio and Concentration on Reaction Time and Yield.

Entry	HOBz [eq]	Buffer Ratio (HOBz : KOAc)	$Pd(OAc)_2$ [mol%]	Reaction Time [min]	Yield [%]
1	1	1 : 2	2	70	38
2	1	1 : 2	-	70	42
3	0.5	1 : 2	-	70	45
4	0.25	1 : 2	-	70	40
5	1	1 : 1	-	105	26
6	KOAc [2 eq]	0 : 2	-	45	26

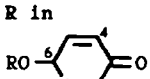
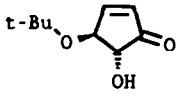
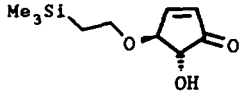
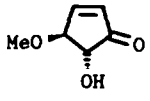
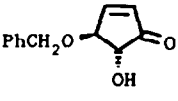
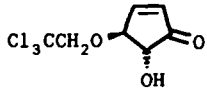
Reaction conditions: A stirred solution of 6-methoxy-2,3-dihydro-6*H*-pyran-3-one[1,2] **1c** (0.39 mmol) and the buffer in dry redistilled DMF (10 mL) was heated to 80°C under N_2. After all the starting material had been consumed (TLC control), the mixture was concentrated *in vacuo* and chromatographed (silica gel, ether/ light petroleum, 4:1), giving cyclopentenone **2c** (cf. Table II, entry **c**).

The experiments showed no significant dependence of yield (40 - 45%) and reaction time (70 min) on buffer concentration, when buffer ratios were held constant (entries 2 - 4). Reproducibility of yield and reaction time were remarkable. Under the new conditions [$PhCO_2H$ (0.5 eq), KOAc (1 eq),

DMF, 80°C] a variation in scale did not cause a drop in yield. We therefore regard process **1** → **2** as optimized.

Influence of Alkoxy Substituent. Attempted preparation of acetal **1** (RO = PhO) via the benzoate route[1,2] failed, presumably due to the leaving ability of phenoxide (pK_a of PhOH ca. 10). Furthermore, the isolation of benzyl alcohol as a side product of the rearrangement of **1d** (cf. Table II, entry **d**) suggested that even benzyloxide functioned as a leaving group under these conditions. We therefore turned to 2-(trimethylsilyl)ethyl protection of the acetal (Table II, entry **b**) and were pleased to find that yields increased to 56%. The dependence of yield on acidity of the derived alcohol ROH was corroborated by the observation that 2,2,2-trichloroethyl derivative **1e** (cf. Table II, entry **e**) gave exclusive decomposition.

Table II. Effect of Leaving Ability of 6-Alkoxy Group.

Entry	R in  **1**[a]	*trans*-4-Alkoxy-5-hydroxy-2-cyclopenten-1-one (**2**) Obtained	Yield [%]
a	t-Bu	 **2a**	60[b]
b	$Me_3SiCH_2CH_2$	 **2b**	56[c], 56[d], 41[e]
c	Me	 **2c**	45[c], 42[d]
d	$PhCH_2$	 **2d**	24[b,f]
e	Cl_3CCH_2	 **2e**	0[d]

[a] 6-Alkoxy-pyranones **1** were prepared from 6-benzoyloxy-2,3-dihydro-6*H*-pyran-3-one and the corresponding alcohol in the presence of $ZnCl_2 \cdot OEt_2$ (10 mol%)[1-3]; [b] $nBu_4N^+Cl^-$ (1 eq), $NaHCO_3$ (5 eq), $Pd(OAc)_2$ (2 mol%), DMF, 80°C; [c] Optimized conditions: $PhCO_2H$ (0.5 eq), KOAc (1 eq), DMF, 80°C; [d] $Et_3N^+CH_2Ph\ Cl^-$ (1 eq), $NaHCO_3$ (5 eq), $Pd(OAc)_2$ (2 mol%), DMF, 80°C; [e] $nBu_4N^+Cl^-$ (1 eq), $NaHCO_3$ (5 eq), $Pd(OAc)_2$ (2 mol%), MeCN, reflux; [f] Benzyl alcohol was isolated as side product (~ 29%).

Table III. Substituent Effects on the Ring Contraction 1 → 2.

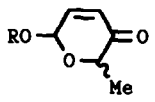
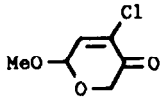
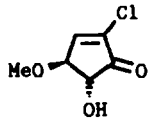
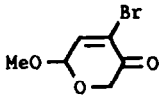
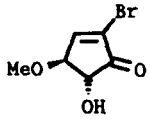
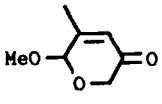
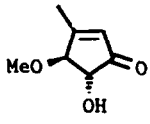
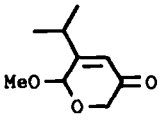
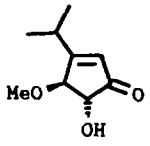
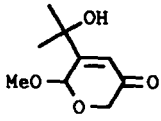
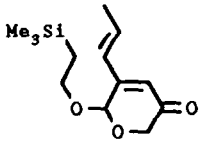
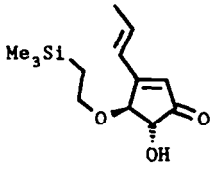
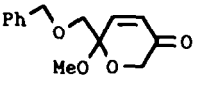
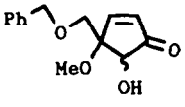
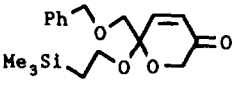
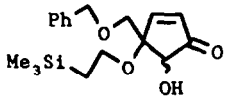
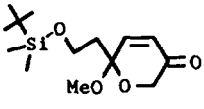
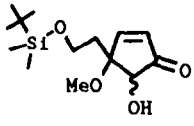
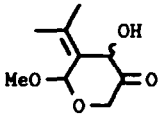
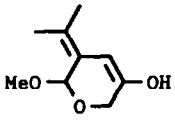
Entry	Substituted 6-Alkoxy-2,3-dihydro-6*H*-pyran-3-one (1)	Product 2	Yield [%]
f	 1f[a] R = Me, Et	--	0[b,c]
g	 1g[d]		26[c]
h	 1h[d]		24[c]
i	 1i		30[e,f]
j	 1j	 +  + 4	
		2j, 10[g]	3, 9[g] 12[g,h]
k	 1k[i]		14[b], 12[e]
l	 1l[j]		66[b,k]
m	 1m		69[b,l]
n	 1n		37[b,m]

Table III, footnotes:
[a]Pyranone **1f** was prepared from 1-(furan-2-yl)ethanol[4]; [b]Optimized conditions: $PhCO_2H$ (0.5 eq), KOAc (1 eq), DMF, 80°C; [c]$nBu_4N^+Cl^-$ (1 eq), $NaHCO_3$ (5 eq), $Pd(OAc)_2$ (2 mol%), DMF, 80°C; [d]For synthesis of 4-halo-pyranones **1g** and **1h** see ref. 5; [e]$Et_3N^+CH_2Ph\ Cl^-$ (1 eq), $NaHCO_3$ (5 eq), $Pd(OAc)_2$ (2 mol%), DMF, 80°C; [f]Starting material **1i** (20%) recovered; [g]$Et_3N^+CH_2Ph\ Cl^-$ (1 eq), $NaHCO_3$ (5 eq), DMF, 80°C; [h]Product **4** is tentatively identified by ^1H NMR and IR data as  ; [i]For preparation of **1k** see ref. 6; [j]For synthesis of **1l** see ref. 7; [k]Diastereomeric ratio 22 : 1; [l]Diastereomeric ratio ~95 : 5; [m]Diastereomeric ratio 20 : 1.

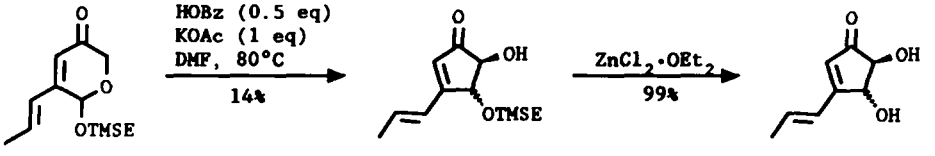
Substituent Effects. Even under optimized conditions the rearrangement reaction of 2-methyl derivative **1f** failed (Table III, entry **f**). Methylation at C-5 (cf. Table III, entry **i**) caused a comparatively small decrease in yield (30% vs. 42% for **1c** under the same reaction conditions; cf. Table II). However, the more bulky isopropyl substituent led to formation of two side products **3** and **4**, presumably due to oxidation of the electron-rich dienol **5**. Cyclopentenone **2j** was isolated albeit only in 10% yield. The



5

yield of the ring contraction of 6-substituted pyranone **1l** (cf. Table III, entry **l**) was surprisingly high (66%). A further slight improvement was accomplished with the 2-(trimethylsilyl)ethoxy derivative **1m** (69%, Table III, entry **m**), in accord with the earlier observations of Table II.
The cyclopentenones prepared by us are widely applicable in natural products syntesis, e.g. for terrein, trichothecenes and prostaglandins.
Rearrangement of E-1-propenyl derivative **1k** (Table III) provides direct access to mould metabolite terrein[6] (**6**) (Scheme 1), which was previously

Scheme 1. Short Route to Mould Metabolite Terrein (**6**).



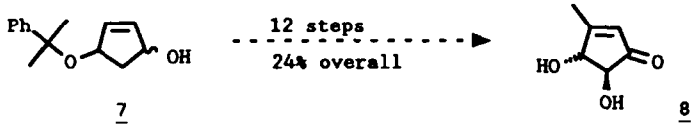
1k **2k** (±)-terrein (**6**)

TMSE = 2-(trimethylsilyl)ethyl

synthesized by four independent groups.[8-10] Although the key step **1k** → **2k** proceeded in low yield (14%), the synthesis is flexible and can be extended to structural analogs.

Recently, 4-cumyloxy-2-cyclopentenol (**7**) has been transformed, by a multistep sequence, into *trans*-4,5-dihydroxy-3-methyl-2-cyclopenten-1-one (**8**), which functioned as a precursor of trichothecenes (Scheme 2).[11] In comparison, the ring contraction of **1i** gave monomethyl ether **2i** in 30% yield (Table III, entry i). Since this reaction is compatible with protecting groups other than methyl (cf. Table II), our one step route to protected 3-methylcyclopentenones compares favorably with the work in the literature (Scheme 2).[11]

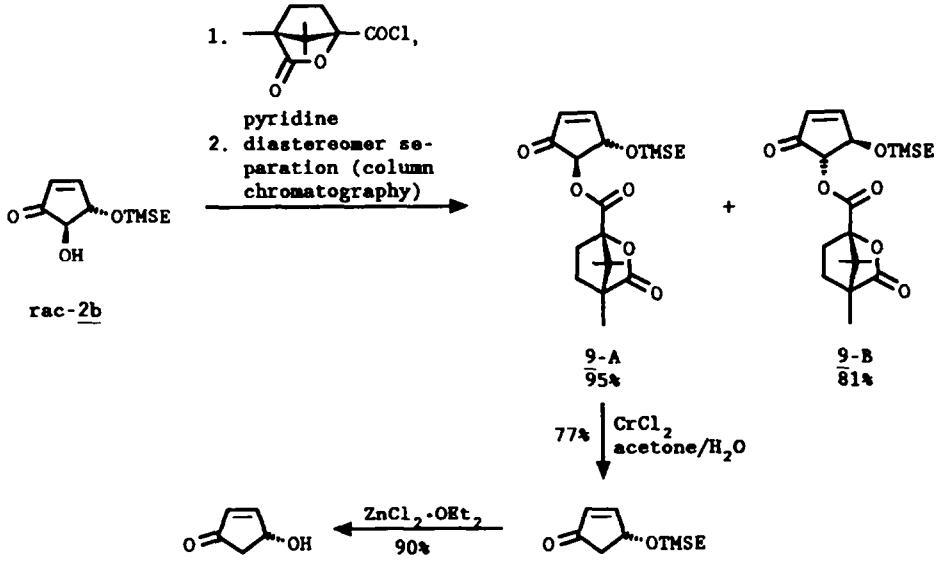
Scheme 2. Construction of C-Ring Fragment of Trichothecenes.[11]



7 8

(+)-R-4-Hydroxy-2-cyclopenten-1-one [(+)-**10**], a key intermediate of prostaglandin synthesis, has been prepared by many routes.[12] The high yielding three step synthesis of optically pure **10** (Scheme 3) demonstrates the

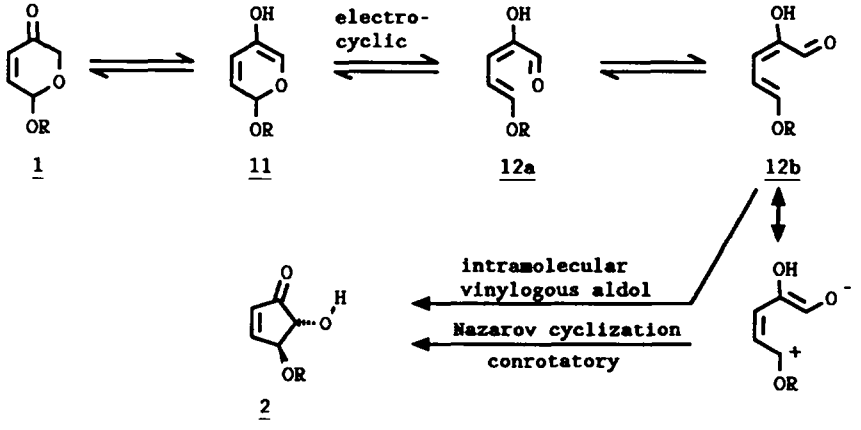
Scheme 3. Synthesis of a Prostaglandin Building Block (+)-R-4-Hydroxy-2-cyclopenten-1-one [(+)-**10**].[13]



utility of the monoprotected cyclopentenones **2a-d**. The measured optical rotation of (+)-**10** ($[\alpha]_D^{22}$ = +94.2° ± 2.8°; c 0.74, methanol) is in excellent agreement with the value given by Rickards and Gill[12c] ($[\alpha]_D^{22}$ = +96°; c 0.118, methanol).

Mechanistic Considerations. The observed independence of reaction rate and product yield on the buffer concentration (Table I) suggests specific acid catalysis for the ring contraction of **1** to **2**. Therefore, enolization of **1** is probably faster than subsequent electrocyclic opening of oxacyclohexadiene **11**. Ring closure of **12b** to **2** can be regarded as either an aldol or a Nazarov type process (Scheme 4). The failure of 2-alkylated pyranone **1f** to rearrange can be attributed to the reduced reactivity of a ketone compared with an aldehyde intermediate (cf. **12**).

Scheme 4.



Conclusions. An investigation of the ring contraction **1** → **2** has shown that homogeneous conditions shorten reaction times and substantially improve reproducibility and yield. The process can therefore be regarded as optimized. Scope and limitations with respect to the substitution pattern of the alkoxy-oxacyclohexenone **1** have been explored. The experiments reveal a clear trend of increase in product yield with decrease in leaving ability of the 6-alkoxy group (cf. Table II). Best results were obtained with the 2-(trimethylsilyl)ethyl protecting group. The potential of the resulting cyclopentenones **2** in natural product synthesis has been demonstrated. Cyclopentenones such as **21-n** contain *four* oxygen functions which are *differentiated* and, therefore, can be manipulated selectively.

EXPERIMENTAL

Melting points: uncorrected, Büchi apparatus.- Infrared spectra: Perkin-Elmer 1710 spectrometer.- ^{1}H NMR spectra: At 80 and 200 MHz, Bruker WP 80 or WP 200 SY spectrometer, solvent $CDCl_3$ unless stated otherwise.- ^{13}C NMR: Bruker WP 200 SY or Bruker AM 300 at 50.3 MHz or 75.5 MHz.- MS: Low and high resolution electron impact mass spectra, Finnigan MAT 312 spectrometer, 70 eV, room temperature, unless otherwise stated. Relative intensities in parantheses.- Optical rotations: Perkin-Elmer 241 polarimeter.- Microanalyses: Department of Organic Chemistry of the University of Hannover.- Preparative column chromatography: J.T. Baker silica gel (particle size 30 -60 μm).- Analytical tlc: Aluminium-backed 0.2 mm silica gel 60 F_{254} plates (E. Merck).- THF and diethyl ether (ether) were distilled from sodium benzophenone ketyl prior to use, CH_2Cl_2 from P_4O_{10}. Petrol refers to light petroleum, bp 30 - 60°C, redistilled prior to use.

4-Benzeneselenenyl-6-methoxy-2,3-dihydro-6H-pyran-3-one. Pyridine (0.69 mL, 8.55 mmol) was added to a stirred solution of PhSeCl(1.57 g, 8.2 mmol) in CH_2Cl_2 (20 mL) under N_2. After 10 min the orange solution was added by syringe to a solution of 6-methoxy-2,3-dihydro-6*H*-pyran-3-one[1,2] **1c** (1 g, 7.8 mmol) in CH_2Cl_2 (34 mL) under N_2. After the reaction had gone to completion (4.5 h, TLC control), the mixture was diluted with CH_2Cl_2 and washed with water (3x). The aqueous phase was reextracted with CH_2Cl_2 and the combined organic layers were dried ($MgSO_4$) and evaporated *in vacuo*. Purification of the residual orange oil (2.47 g) by column chromatography on silica gel (80 g, ether/petrol, 4 : 6) afforded the title compound (1.59 g, yellowish amorphous solid), which according to ^{1}H NMR data contained ~10% (w/w) 4-chloro-6-methoxy-2,3-dihydro-6*H*-pyran-3-one.[14] Yield, calculated for the pure benzeneselenenyl-pyranone, was 65%. IR (KBr) ν 3050, 2926, 2876, 2825, 1679, 1605, 1579, 1333, 1137, 1061, 963, 747 cm^{-1}; 90 MHz ^{1}H NMR δ 7.71 - 7.52 (m, 2 H, aryl H), 7.49 - 7.3 (m, 3 H, aryl H), 6.17 (d, $J_{5,6}$ = 3.8 Hz, 1 H, H-5), 4.96 (d, $J_{5,6}$ = 3.8 Hz, 1 H, H-6), 4.56 (d, ^2J = 16.5 Hz, 1 H, H-2), 4.19 (d, ^2J = 16.5 Hz, 1 H, H-2), 3.43 (s, 3 H, OCH_3); *m/z* 284 (M^+, ^{80}Se, 48), 282 (M^+, ^{78}Se, 24), 253 (M^+-CH_3O, ^{80}Se, 44), 251 (M^+-CH_3O, ^{78}Se, 21), 242 (10), 211 (9), 182 (70), 180 (37), 173 (56), 157 (48), 155 (26), 127 (100), 115 (65), 77 (74). Exact mass calcd for $C_{12}H_{12}O_3{}^{80}$Se 283.9952, found 283.9952.

6-Methoxy-5-methyl-2,3-dihydro-6H-pyran-3-one (**1i**). Methyllithium (2.6 mL of a 1.6 M solution in ether, 4.16 mmol) was added, dropwise and with stirring, to a suspension of $CuBr{\cdot}SMe_2$ (435 mg, 2.12 mmol) in anhydrous ether (3.1 mL) at -50°C under argon. After 45 min the greenish solution of the organocuprate was cooled to -78°C, and a solution of 4-benzeneselene-

nyl-6-methoxy-2,3-dihydro-6*H*-pyran-3-one (400 mg, 1.41 mmol) in dry ether (1.8 mL) was added dropwise during 15 min, while the temperature was maintained at -78°C. After a further 60 min the reaction was quenched by adding slowly sat. aq. NH_4Cl solution (Caution! Evolution of methane!). The mixture was diluted with ether (15 mL), the organic phase separated and washed twice with sat. aq. NH_4Cl/1.7 M NH_3 (2 : 1). The combined aqueous layers were extracted with ether (3x) and the combined extracts were dried ($MgSO_4$). After removal of the solvent *in vacuo* the residue (400 mg) was filtered through silica gel (7 g, ether/petrol, 3 : 7) to yield crude 4-benzeneselenenyl-6-methoxy-5-methyltetrahydro-2*H*-pyran-3-one (360 mg, yellow oil).

3-Phenyl-2-(*p*-toluenesulfonyl)oxaziridine[15] (365 mg, 1.33 mmol) was added to a stirred solution of the crude 4-benzeneselenenyltetrahydropyranone (360 mg, 1.2 mmol) and pyridine (0.49 mL, 6.07 mmol) in $CHCl_3$ (1.7 mL). After 75 min the volatiles were evaporated *in vacuo* and the residual orange oil (740 mg) was purified by column chromatography on silica gel (40 g, CH_2Cl_2) to give 5-methylpyranone **1i** (96 mg, 48%, colorless oil). IR (cap film) ν 2937, 2915, 2893, 2833, 1712, 1681, 1647, 1441, 1266, 1110, 1067, 960, 857 cm^{-1}; 200 MHz ^1H NMR (CD_2Cl_2) δ 5.89 (q, ^4J = 1.4 Hz, 1 H, H-4), 4.90 (s, 1 H, H-6), 4.31 (d, ^2J = 16 Hz, 1 H, H-2), 3.97 (d, ^2J = 16 Hz, 1 H, H-2), 3.50 (s, 3 H, OCH_3), 1.98 (d, ^4J = 1.4 Hz, 3 H, CH_3); 50.3 MHz ^{13}C NMR (CD_2Cl_2) δ 194.71 (s, C-3), 157.3 (s, C-5), 124.66 (d, C-4), 98.09 (d, C-6), 65.39 (t, C-2), 57.03 (q, OCH_3), 20.03 (q, CH_3); *m/z* 142 (M^+, 7.5), 127 (M^+-CH_3, 1.6), 112 (M^+-CH_2O, 100), 111 (M^+-OCH_3, 34), 97 (63), 69 (42). Exact mass calcd for $C_7H_{10}O_3$ 142.0630, found 142.0630.

5-Isopropyl-6-methoxy-2,3-dihydro-6H-pyran-3-one (**1j**). Isopropylmagnesium bromide (6.2 mL of a 1 M solution in THF) was added to a stirred suspension of $CuBr \cdot SMe_2$ (180 mg, 0.88 mmol) in anhydrous THF (1 mL) at -10°C under N_2, causing the formation of a black semisolid mixture. A solution of 4-benzeneselenenyl-6-methoxy-2,3-dihydro-6*H*-pyran-3-one (500 mg, 1.76 mmol) in dry THF (2 mL) was added dropwise and with stirring. After 30 min at -10°C the mixture was allowed to warm slowly during 105 min to r.t. The reaction was then recooled to 0°C and quenched with sat. aq. NH_4Cl solution (Caution! Evolution of propane!). After diluting the mixture with ether (15 mL), the organic phase was separated and washed twice with sat. aq. NH_4Cl/1.7 M NH_3 (2 : 1). The combined aqueous layers were extracted with ether (3x) and the combined extracts were washed with brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue (530 mg) was filtered through silica gel (8 g, ether/petrol, 2 : 8) to give crude 4-benzeneselenenyl-5-isopropyl-6-methoxy-tetrahydro-2*H*-pyran-3-one (355 mg, yellow oil).

3-Phenyl-2-(*p*-toluenesulfonyl)oxaziridine[15] (345 mg, 1.25 mmol) was added to a stirred solution of the crude 4-benzeneselenenyltetrahydropyranone (355 mg, 1.08 mmol) and pyridine (0.44 mL, 5.45 mmol) in $CHCl_3$ (1.5 mL). After 60 min the solvent was evaporated *in vacuo* and the residual orange oil (800 mg) was purified by column chromatography on silica gel (22 g, CH_2Cl_2) to yield 5-isopropylpyranone **1j** (75 mg, 25%, slightly yellow oil). IR (cap film) ν 2968, 2935, 2900, 2832, 1710, 1685, 1637, 1467, 1280, 1267, 1063, 965, 884, 860 cm^{-1}; 200 MHz ^1H NMR (CD_2Cl_2) δ 5.89 (d, ^4J = 1.5 Hz, 1 H, H-4), 5.01 (s, 1 H, H-6), 4.33 (d, ^2J = 17 Hz, 1 H, H-2), 3.99 (d, ^2J = 17 Hz, 1 H, H-2), 3.50 (s, 3 H, OCH_3), 2.50 (d septet, ^3J = 7 Hz, ^4J = 1.5 Hz, 1 H, $(CH_3)_2CH$), 1.14 (d, ^3J = 7 Hz, 6 H, $(CH_3)_2CH$); 50.3 MHz ^{13}C NMR (CD_2Cl_2) δ 195.44 (s, C-3), 166.34 (s, C-5), 121.66 (d, C-4), 96.94 (d, C-6), 65.54 (t, C-2), 56.88 (q, OCH_3), 32.07 (d, $(CH_3)_2CH$), 21.22 (q, CH_3), 20.72 (q, CH_3); *m/z* 170 (M^+, 3.7), 155 (M^+-CH_3, 2.2), 140 (M^+-CH_2O, 100), 139 (M^+-OCH_3, 39), 125 (61), 97 (38). Exact mass calcd for $C_9H_{14}O_3$ 170.0943, found 170.0944.

6-Benzoyloxy-6-benzyloxymethyl-2,3-dihydro-6H-pyran-3-one. A solution of benzoyl chloride (0.82 mL, 7.06 mmol) in dry CH_2Cl_2 (3 mL) was added dropwise to a stirred solution of 6-benzyloxymethyl-6-hydroxy-2,3-dihydro-6*H*-pyran-3-one[7] (1.5 g, 6.41 mmol) and pyridine (1.3 mL, 16.1 mmol) in anhydrous CH_2Cl_2 (6.5 mL) at 0°C. The mixture was stirred at 0°C for 30 min, then allowed to warm to r.t. After the reaction had gone to completion (5 h, TLC control), the mixture was diluted with ether (30 mL) and washed with water (2x). The aqueous phase was reextracted with ether and the combined organic layers were dried ($MgSO_4$) and evaporated *in vacuo*. Column filtration of the residual brown oil (2.6 g) through silica gel (55 g, ether/petrol, 4 : 6) and subsequent purification by column chromatography (35 g silica gel, ether/petrol, 3 : 7) afforded the benzoate (950 mg, 44%, yellowish oil). IR ($CHCl_3$) ν 3070, 2928, 2871, 1713, 1601, 1586, 1496, 1453, 1276, 1108, 910, 868 cm^{-1}; 200 MHz ^1H NMR δ 8.06 - 7.93 (m, 2 H, aryl H), 7.62 - 7.36 (m, 3 H, aryl H), 7.42 (d, $J_{4,5}$ = 10.3 Hz, H-5), 7.29 (m, 5 H, aryl H), 6.25 (d, $J_{4,5}$ = 10.3 Hz, H-4), 4.72 (d, ^2J = 16.8 Hz, 1 H, H-2), 4.64 (s, 2 H, $PhCH_2$), 4.36 (d, ^2J = 16.8 Hz, 1 H, H-2), 4.14 (d, ^2J = 10 Hz, 1 H, BnOCHH), 3.93 (d, ^2J = 10 Hz, 1 H, BnOCHH); 50.3 MHz ^{13}C NMR δ 193.58 (s, C-3), 164.71 (s, $PhCO_2$), 144.65 (d, C-5), 137.31 (s, aryl C), 133.56 (d, aryl C), 129.83 (d, 2 C, aryl C), 129.51 (s, aryl C), 128.52 (d, 2 C, aryl C), 128.45 (d, 2 C, aryl C), 127.92 (d, aryl C or C-4), 127.77 (d, 2 C, aryl C), 127.66 (d, C-4 or aryl C), 99.10 (s, C-6), 73.88 (t, $PhCH_2$), 72.00 (t, $BnOCH_2$), 68.05 (t, C-2); *m/z* (50°C) 338 (M^+, 0.4), 308 (M^+-CH_2O, 0.3), 217 (3), 122 (15), 110 (21), 105 (100), 91 (92), 77 (40).

6-Benzyloxymethyl-6-(2-trimethylsilylethoxy)-2,3-dihydro-6H-pyran-3-one (**1m**). $ZnCl_2 \cdot OEt_2$ (0.1 mL of a 2.2 M solution in CH_2Cl_2, Merck, 0.22 mmol) was added to a solution of 6-benzoyloxy-6-benzyloxymethyl-2,3-dihydro-6*H*-pyran-3-one (710 mg, 2.1 mmol) and 2-(trimethylsilyl)ethanol (0.45 mL, 3.15 mmol) in dry 1,2-dichloroethane (4.6 mL) at r.t. under N_2. After all the starting material had been consumed (45 min, TLC control), the reaction was quenched with sat. aq. $NaHCO_3$ solution. The aqueous layer was extracted with CH_2Cl_2 (3x) and the combined organic layers were washed with aq. $NaHCO_3$ solution, dried ($MgSO_4$) and evaporated *in vacuo*. Purification of the yellow residue (800 mg) by column chromatography on silica gel (25 g, ether/petrol, 2 : 8) gave 2-(trimethylsilyl)ethoxy derivative **1m** (625 mg, 89%, colorless oil. IR (cap film) ν 3065, 3032, 2953, 2882, 1698, 1630, 1455, 1289, 1249, 1107, 1053, 1010, 861, 839, 699 cm^{-1}; 200 MHz ^1H NMR δ 7.33 (m, 5 H, aryl H), 7.05 (d, $J_{4,5}$ = 10.2 Hz, 1 H, H-5), 6.13 (d, $J_{4,5}$ = 10.2 Hz, 1 H, H-4), 4.65 (d, ^2J = 12 Hz, 1 H, PhC*H*H), 4.54 (d, ^2J = 12 Hz, 1 H, PhCH*H*), 4.39 (d, ^2J = 17 Hz, 1 H, H-2), 4.16 (d, ^2J = 17 Hz, 1 H, H-2), 3.73 (d, ^2J = 10 Hz, 1 H, BnOC*H*H), 3.63 (m, 2 H, $CH_2CH_2SiMe_3$), 3.50 (d, ^2J = 10 Hz, 1 H, BnOCH*H*), 0.93 (m, 2 H, $CH_2CH_2SiMe_3$), 0.02 (s, 9 H, $SiMe_3$); 50.3 MHz ^{13}C NMR δ 194.41 (s, C-3), 147.10 (d, C-5), 137.23 (s, aryl C-1), 128.36 (d, aryl C-2,6), 127.85 (d, aryl C-4), 127.76 (d, aryl C-3,5), 127.08 (d, C-4), 95.34 (s, C-6), 73.48 (t, $PhCH_2$), 70.48 (t, BnO-CH_2), 66.77 (t, C-2), 59.98 (t, $CH_2CH_2SiMe_3$), 18.27 (t, $CH_2CH_2SiMe_3$), -1.5 (q, $SiMe_3$); *m/z* 304 (M^+-CH_2O, 0.2), 217 (3.3), 200 (4), 185 (37), 165 (3), 157 (3), 129 (14), 91 (100), 75 (13), 73 (89).

6-(2-t-Butyldimethylsilyloxyethyl)-6-hydroxy-2,3-dihydro-6H-pyran-3-one. 5-(2-*t*-Butyldimethylsilyloxyethyl)-2-hydroxymethylfuran[16] (250 mg, 0.98 mmol) and potassium acetate (191 mg, 1.95 mmol) were dissolved in THF/H_2O (2.5 mL, 4 : 1) and cooled to -18°C. N-Bromosuccinimide (NBS) (180 mg, 1 mmol) was added in small portions to the vigorously stirred mixture. Every new portion of NBS was added after the color of bromine from the previous addition had faded. A persistant yellow color indicated the end of the reaction. Excess oxidant was reduced by adding solid Na_2SO_3 (~ 100 mg) and allowing to warm to r.t. Anhydrous $MgSO_4$(~ 750 mg) was added to bind water and the mixture was transferred onto a columnn with silica gel (15 g). Elution with ether/petrol (1 : 1) gave the title pyranone (245 mg, 92%, slightly yellow oil). IR ($CHCl_3$) ν 3387, 2958, 2932, 2887, 2860, 1703, 1689, 1631, 1472, 1262, 1078, 898, 862, 840 cm^{-1}; 200 MHz ^1H NMR δ 6.77 (d, $J_{4,5}$ = 10 Hz, 1 H, H-5), 5.97 (dd, $J_{4,5}$ = 10 Hz, $^4J_{2,4}$ = 0.8 Hz, 1 H, H-4), 5.65 (s, 1 H, OH), 4.62 (d, ^2J = 16.5 Hz, 1 H, H-2), 4.24 (ddd, ^2J = 10.2 Hz, J = 11.2 Hz, J = 2.6 Hz, 1 H, TBDMSOC*H*HCH$_2$), 4.06 (dd, ^2J = 16.5 Hz, $^4J_{2,4}$ = 0.8 Hz, 1 H, H-2), 3.81 (ddd, ^2J = 10.2 Hz, J = 4.3 Hz, J = 3

Hz, 1 H, TBDMSOCH*H*CH_2), 2.12 (ddd, ^2J = 14 Hz, J = 11.2 Hz, J = 4.3 Hz, 1 H, TBDMSOCH$_2$C*H*H), 1.82 (ddd, ^2J = 14 Hz, J = 3 Hz, J = 2.6 Hz, 1 H, TBDMSOCH$_2$CH*H*), 0.88 (s, 9 H, *t*-butyl), 0.09 (s, 3 H, CH_3Si), 0.08 (s, 3 H, CH_3-Si); 50.3 MHz ^{13}C NMR δ 195.54 (s, C-3), 148.73 (d, C-5), 125.78 (d, C-4), 93.77 (s, C-6), 66.31 (t, C-2), 59.53 (t, TBDMSOCH_2CH_2), 39.52 (t, TBDMSO-CH_2CH_2), 25.65 (q, 3 C, $C(CH_3)_3$), 17.95 (s, $C(CH_3)_3$), -5.70 (q, CH_3Si), -5.80 (q, CH_3Si); *m/z* 257 (M^+-CH_3, 0.2), 242 (M^+-CH_2O, 1.8), 215 (M^+-^{t}butyl, 7), 197 (8), 185 (22), 167 (9.5), 157 (11), 123 (25), 105 (20), 95 (18), 75 (100), 57 (27). Exact mass calcd for $C_{12}H_{22}O_3Si$ (M^+-CH_2O) 242.1338, found 242.1337.

6-(2-t-Butyldimethylsilyloxyethyl)-6-methoxy-2,3-dihydro-6H-pyran-3-one (**1n**). Silver oxide (260 mg, 1.12 mmol) was added to a vigorously stirred solution of 6-(2-t-butyldimethylsilyloxyethyl)-6-hydroxy-2,3-dihydro-6*H*-pyran-3-one (100 mg, 0.367 mmol) in dry ether (1.4 mL) under N_2, followed by methyl iodide (0.08 mL, 1.29 mmol). After 29 h the mixture was filtered, concentrated *in vacuo* at r.t. and purified by column chromatography on silica gel (6 g, ether/petrol, 4 : 6) to give the starting material (16 mg) and methoxy derivative **1n** (55 mg, 52%, colorless oils). IR (cap film) *ν* 2957, 2932, 2885, 2858, 1703, 1631, 1473, 1388, 1256, 1105, 838, 778 cm^{-1}; 200 MHz ^{1}H NMR δ 7.01 (d, $J_{4,5}$ = 10 Hz, 1 H, H-5), 6.06 (dd, $J_{4,5}$ = 10 Hz, $^4J_{2,4}$ = 0.4 Hz, 1 H, H-4), 4.35 (d, ^2J = 16.5 Hz, 1 H, H-2), 4.11 (dd, ^2J = 16.5 Hz, $^4J_{2,4}$ = 0.4 Hz, 1 H, H-2), 3.74 (m, 2 H, TBDMSOC*H*$_2$CH$_2$), 3.33 (s, 3 H, OCH_3), 2.15 (dt, J_t = 6.2 Hz, J_d = 14.2 Hz, 1 H, TBDMSOCH$_2$-C*H*H), 2.0 (dt, J_t = 6.2 Hz, J_d = 14.2 Hz, 1 H, TBDMSOCH$_2$CH*H*), 0.88 (s, 9 H, t-butyl), 0.04 (s, 3 H, CH_3Si), 0.03 (s, 3 H, CH_3Si); 50.3 MHz ^{13}C NMR δ 194.60 (s, C-3), 149.18 (d, C-5), 126.32 (d, C-4), 96.27 (s, C-6), 66.74 (t, C-2), 58.46 (t, TBDMSOCH_2CH_2), 49.79 (q, OCH_3), 38.33 (t, OTBDMSOCH$_2$-CH_2), 25.83 (q, 3 C, $C(CH_3)_3$), 18.17 (s, $C(CH_3)_3$), -5.49 (q, CH_3Si), -5.52 (q, CH_3Si); *m/z* 286 (M^+, 0.07), 271 (M^+-CH_3, 0.2), 256 (M^+-CH_2O, 0.8), 255 (M^+- CH_3O, 1.9), 229 (M^+-^{t}butyl, 13), 199 (27), 197 (23), 181 (7.5), 169 (14), 167 (17.5), 123 (27), 119 (22), 89 (100), 75 (43). Exact mass calcd for $C_{13}H_{23}O_3Si$ (M^+-CH_3O) 255.1417, found 255.1417.

General Procedure for the Ring Contraction of 6-Alkoxy-2,3-dihydro-6H-pyran-3-ones **1** *under Optimized Conditions.* Benzoic acid (0.5 eq) and potassium acetate (1 eq) were added to a solution of pyranone **1** in dry redistilled DMF under N_2. The mixture was stirred at 80°C until TLC showed absence of starting material and then concentrated *in vacuo* at the same temperature. Further work up was carried out either anhydrous by column chromatography of the brown residue on silica gel, eluting with ether/petrol, or aqueous by partitition of the residue between ether/aq. $NaHCO_3$ solution (5%), followed by extraction of the aqueous phase with ether

(3x). The combined organic layers were washed with brine, dried ($MgSO_4$), evaporated *in vacuo* and purified by column chromatography on silica gel (ether/petrol) to give cyclopentenone **2** as an oil.

trans-5-Hydroxy-4-(2-trimethylsilylethoxy)-2-cyclopenten-1-one (**2b**). The reaction of pyranone **1b** (283 mg, 1.32 mmol) in DMF (34 mL) in the presence of HOBz (80 mg, 0.655 mmol) and KOAc (128.5 mg, 1.31 mmol) (80°C, 135 min), followed by aqueous work up, gave cyclopentenone **2b** (159 mg, 56%, slightly yellow oil) identical to the literature.[6]

trans-5-Hydroxy-4-methoxy-2-cyclopenten-1-one (**2c**). The ring contraction of pyranone **1c** (50 mg, 0.39 mmol) in DMF (10 mL) with HOBz (24 mg, 0.2 mmol) and KOAc (38 mg, 0.39 mmol) (80°C, 70 min), followed by anhydrous work up, afforded cyclopentenone **2c** (23 mg, 45%, yellowish oil). IR (cap film) ν 3560, 3400, 3000, 2940, 1725, 1660, 1450, 1370, 1320, 1120, 1080, 1035, 975 cm^{-1}; 200 MHz ^1H NMR δ 7.51 (dd, $J_{2,3}$ = 6 Hz, $J_{3,4}$ = 2 Hz, 1 H, H-3), 6.30 (dd, $J_{2,3}$ = 6 Hz, $J_{2,4}$ = 2 Hz, 1 H, H-2), 4.38 (m, 1 H, H-4), 4.21 (d, $J_{4,5}$ = 2.5 Hz, 1 H, H-5), 3.60 (s, 3 H, OCH_3), 3.29 (bs, 1 H, OH); 75 MHz ^{13}C NMR δ 204.37 (s, C-1), 158.53 (d, C-3), 132.20 (d, C-2), 84.65 (d, C-5), 79.94 (d, C-4), 58.00 (q, OCH_3); *m/z* 128 (M^+, 31), 100 (28), 97 (31), 89 (100), 81 (23), 68 (40), 59 (72). Exact mass calcd for $C_5H_5O_2$ (M^+-OCH_3) 97.0289, found 97.0289.

trans-5-Hydroxy-3-(E-1-propenyl)-4-(2-trimethylsilylethoxy)-2-cyclopenten-1-one (**2k**). Pyranone **1k** (44 mg, 0.17 mmol) in DMF (4.4 mL) was allowed to react in the presence of HOBz (10.6 mg, 0.087 mmol) and KOAc (17 mg, 0.17 mmol) (80°C, 14 h). Aqueous work up afforded starting material **1k** (4.7 mg, 11%) and cyclopentenone **2k** (6 mg, 14%, slightly yellow oil), identical to the literature.[6]

4-Benzyloxymethyl-5-hydroxy-4-methoxy-2-cyclopenten-1-one (**2l**). The reaction of pyranone **1l** (280 mg, 1.13 mmol) in DMF (29 mL) in the presence of HOBz (69 mg, 0.565 mmol) and KOAc (110 mg, 1.21 mmol) (80°C, 195 min), followed by anhydrous work up, gave cyclopentenone **2l** (185 mg, 66%, 22 : 1 mixture of diastereomers). IR (cap film) ν 3441, 3065, 3031, 2936, 2867, 2838, 1724, 1588, 1455, 1363, 1114, 1029, 741, 700 cm^{-1}; 200 MHz ^1H NMR, major isomer δ 7.43 (d, $J_{2,3}$ = 6 Hz, 1 H, H-3), 7.4 - 7.17 (m, 5 H, aryl H), 6.39 (d, $J_{2,3}$ = 6 Hz, 1 H, H-2), 4.49 (s, 2 H, $PhCH_2$), 4.35 (s, 1 H, H-5), 3.72 (d, ^2J = 8.5 Hz, 1 H, BnOCHH), 3.65 (d, ^2J = 8.5 Hz, 1 H, BnOCHH), 3.42 (s, 3 H, OCH_3), 3.07 (bs, 1 H, OH); minor isomer δ 6.46 (d, $J_{2,3}$ = 6 Hz, 1 H, H-2), 4.59 (s, 2 H, $PhCH_2$), 4.13 (s, 1 H, H-5), 3.25 (s, 3 H, OCH_3); 50.3 MHz ^{13}C NMR δ 203.29 (s, C-1), 160.19 (d, C-3), 137.45 (s, aryl C-1), 132.82 (d, C-2), 128.38 (d, aryl C-2,6), 127.74 (d, aryl C-4), 127.47 (d, aryl C-3,5), 85.18 (s, C-4), 77.87 (d, C-5), 73.46 (t, $PhCH_2$), 69.43 (t, $BnOCH_2$), 52.33 (q, OCH_3); *m/z* 248 (M^+, 1), 217 (M^+-CH_3O,

8.8), 189 (7.6), 165 (9), 144 (21), 127 (68), 115 (26), 99 (40), 91 (100). Exact mass calcd for $C_{13}H_{13}O_3$ (M^+-CH_3O) 217.0865, found 217.0865.

4-Benzyloxymethyl-5-hydroxy-4-(2-trimethylsilylethoxy)-2-cyclopenten-1-one (**2m**). The ring contraction of pyranone **1m** (558 mg, 1.67 mmol) in DMF (42 mL) with HOBz (102 mg, 0.835 mmol) and KOAc (164 mg, 1.67 mmol) (80°C, 210 min, anhydrous work up) gave cyclopentenone **2m** (386 mg, 69%, ~95 : 5 mixture of diastereomers). IR ($CHCl_3$) ν 3542, 2956, 2871, 1727, 1673, 1455, 1363, 1251, 1109, 861, 839 cm^{-1}; 200 MHz ^1H NMR δ 7.41 (d, $J_{2,3}$ = 6 Hz, 1 H, H-3), 7.38 - 7.15 (m, 5 H, aryl H), 6.38 (d, $J_{2,3}$ = 6 Hz, 1 H, H-2), 4.51 (d, ^2J = 12.6 Hz, 1 H, PhC*H*H), 4.45 (d, ^2J = 12.6 Hz, 1 H, PhCH*H*), 4.35 (s, 1 H, H-5), 3.79 - 3.53 (m, 2 H, OC*H*$_2$CH$_2$SiMe$_3$), 3.72 (d, ^2J = 9.3 Hz, 1 H, BnOC*H*H), 3.65 (d, ^2J = 9.3 Hz, 1 H, BnOCH*H*), 3.02 (bs, 1 H, OH), 0.93 (t, J = 8 Hz, 2 H, OCH$_2$C*H*$_2$SiMe$_3$), 0.01 (s, 9 H, Me$_3$Si); 50.3 MHz ^{13}C NMR δ 203.09 (s, C-1), 160.12 (d, C-3), 137.29 (s, aryl C-1), 132.63 (d, C-2), 128.38 (d, aryl C-2,6), 127.76 (d, aryl C-4), 127.41 (d, aryl C-3, 5), 84.68 (s, C-4), 78.51 (d, C-5), 73.41 (t, PhCH$_2$), 69.41 (t, BnOCH$_2$), 62.02 (t, OCH$_2$CH$_2$SiMe$_3$), 18.87 (t, OCH$_2$CH$_2$SiMe$_3$), -1.35 (q, SiMe$_3$); *m/z* 306 (M^+-C_2H_4, 0.5), 291 (M^+-C_2H_4-CH_3, 0.5), 276 (0.9), 185 (51), 169 (8), 165 (6), 157 (5), 91 (99), 75 (17), 73 (100). Exact mass calcd for $C_{16}H_{22}O_4Si$ (M^+-C_2H_4) 306.1287, found 306.1286.

4-(2-t-Butyldimethylsilyloxyethyl)-5-hydroxy-4-methoxy-2-cyclopenten-1-one (**2n**). The reaction of pyranone **1n** (425 mg, 1.48 mmol) in DMF (38 mL) with HOBz (90 mg, 0.74 mmol) and KOAc (145 mg, 1.48 mmol) (80°C, 4 h, anhydrous work up) afforded cyclopentenone **2n** (160 mg, 37%, 20 : 1 mixture of diastereomers) as a yellowish oil. IR ($CHCl_3$) ν 3369, 2957, 2932, 2885, 2859, 1728, 1471, 1362, 1258, 1092, 904, 839 cm^{-1}; 200 MHz ^1H NMR δ 7.38 (d, $J_{2,3}$ = 6.2 Hz, 1 H, H-3), 6.31 (d, $J_{2,3}$ = 6.2 Hz, 1 H, H-2), 4.27 (bd, $J_{5,OH}$ = 7.6 Hz, 1 H, H-5), 4.0 (bd, $J_{5,OH}$ = 7.6 Hz, 1 H, OH), 3.73 (dt, J_t = 4.2 Hz, J_d = 10 Hz, 1 H, TBDMSOC*H*HCH$_2$), 3.52 (dt, J_t = 10 Hz, J_d = 3.2 Hz, 1 H, TBDMSOCH*H*CH$_2$), 3.39 (s, 3 H, OCH$_3$), 2.21 (ddd, ^2J = 14.5 Hz, J = 10 Hz, J = 4.2 Hz, 1 H, TBDMSOCH$_2$C*H*H), 1.96 (ddd, ^2J = 14.5 Hz, J = 4.2 Hz, J = 3.2 Hz, 1 H, TBDMSOCH$_2$CH*H*), 0.87 (s, 9 H, ^{t}butyl), 0.04 (s, 3 H, CH$_3$Si), 0.035 (s, 3 H, CH$_3$Si); 50.3 MHz ^{13}C NMR δ 203.8 (s, C-1), 161.67 (d, C-3), 131.63 (d, C-2), 84.99 (s, C-4), 78.31 (d, C-5), 58.64 (t, TBDMSOCH$_2$CH$_2$), 51.68 (q, OCH$_3$), 34.78 (t, TBDMSOCH$_2$CH$_2$), 25.75 (q, 3 C, C(CH$_3$)$_3$), 18.07 (s, C(CH$_3$)$_3$), -5.72 (q, CH$_3$Si), -5.87 (q, CH$_3$Si); *m/z* 271 (M^+-CH_3, 0.3), 229 (M^+- ^{t}butyl, 15.5), 197 (57), 167 (100), 139 (5.7), 123 (21), 89 (40), 75 (52), 73 (37). Exact mass calcd for $C_{10}H_{17}O_4Si$ (M^+-^{t}butyl) 229.0896, found 229.0896.

General Procedure for the Ring Contraction of 6-Alkoxy-2,3-dihydro-6H-pyran-3-ones under Heterogenous Conditions. $NaHCO_3$ (5 eq), the phase trans-

fer catalyst (nBu$_4$N$^+$Cl$^-$ or Et$_3$N$^+$CH$_2$Ph Cl$^-$, 1 eq) and Pd(OAc)$_2$ (2 mol%) were added to a solution of pyranone **1** in dry redistilled DMF under N_2. The mixture was stirred at 80°C until TLC showed absence of starting material. The mixture was then concentrated *in vacuo* at 80°C and the resulting dark brown residue purified by column chromatography on silica gel, eluting with ether/petrol, to give cyclopentenone **2** as an oil.

trans-4-t-*Butoxy-5-hydroxy-2-cyclopenten-1-one* (**2a**). The ring contraction of pyranone **1a** (350 mg, 2.05 mmol) in DMF (60 mL) with NaHCO$_3$ (680 mg, 8.2 mmol), nBu$_4$N$^+$Cl$^-$ (570 mg, 2.05 mmol) and Pd(OAc)$_2$ (46 mg, 0.2 mmol) (80°C, 24 h) gave cyclopentenone **2a** (210 mg, 60%) as yellow needles, mp 52.5 - 53°C. IR ($CHCl_3$) ν 3550, 3420, 3000, 2980, 1720, 1585, 1470, 1390, 1370, 1320, 1260, 1185, 1120, 1065, 990, 905 cm^{-1}; 300 MHz ^{1}H NMR δ 7.34 (dd, $J_{2,3}$ = 6 Hz, $J_{3,4}$ = 2 Hz, 1 H, H-3), 6.35 (dd, $J_{2,3}$ = 6 Hz, $J_{2,4}$ = 1.5 Hz, 1 H, H-2), 4.61 (m, 1 H, H-4), 4.10 (d, $J_{4,5}$ = 2.5 Hz, 1 H, H-5), 3.03 (s, 1 H, OH), 1.32 (s, 9 H, ^{t}butyl); 75 MHz ^{13}C NMR δ 205.37 (s, C-1), 161.48 (d, C-3), 131.39 (d, C-2), 80.48 (d, C-5), 76.42 (d, C-4), 75.01 (s, $C(CH_3)_3$), 28.16 (q, $C(CH_3)_3$); *m/z* 114 (89), 97 (36), 96 (90), 69 (22), 68 (23), 57 (100). Exact mass calcd for $C_5H_5O_2$ (M$^+$-^{t}butoxy) 97.0289, found 97.0289.

trans-*4-Benzyloxy-5-hydroxy-2-cyclopenten-1-one* (**2d**). The reaction of pyranone **1d** (188 mg, 0.92 mmol) in DMF (20 mL) in the presence of NaHCO$_3$ (390 mg, 4.64 mmol), nBu$_4$N$^+$Cl$^-$ (256 mg, 0.92 mmol) and Pd(OAc)$_2$ (4.7 mg, 0.021 mmol) (80°C, 8.5 h) gave benzyl alcohol (29 mg, 29%) and cyclopentenone **2d** (45 mg, 24%, slightly yellow oil). IR (cap film) ν 3420, 3060, 3040, 2880, 1725, 1590, 1500, 1455, 1355, 1320, 1210, 1120, 1075, 1040, 1030, 985, 970, 940 cm^{-1}; 90 MHz ^{1}H NMR δ 7.47 (dd, $J_{2,3}$ = 6 Hz, $J_{3,4}$ = 2 Hz, 1 H, H-3), 7.44 - 7.27 (m, 5 H, aryl H), 6.28 (dd, $J_{2,3}$ = 6 Hz, $J_{2,4}$ = 1.5 Hz, 1 H, H-2), 4.89 (d, ^2J = 12 Hz, 1 H, PhC*H*H), 4.74 (d, ^2J = 12 Hz, 1 H, PhCH*H*), 4.56 (m, 1 H, H-4), 4.29 (d, $J_{4,5}$ = 2.5 Hz, 1 H, H-5), 2.98 (bs, 1 H, OH); 75 MHz ^{13}C NMR δ 204.36 (s, C-1), 158.94 (d, C-3), 137.37 (s, aryl C), 132.18 (d, C-2), 128.51 (d, aryl C), 128.02 (aryl C), 82.65 (d, C-5), 80.30 (d, C-4), 72.43 (t, $PhCH_2$); *m/z* 204 (M$^+$, 1), 203 (3), 177 (13), 176 (9), 160 (2), 159 (5), 158 (5), 132 (8), 105 (15), 91 (100), 89 (13), 87 (15), 65 (14), 52 (17). Exact mass calcd for $C_{12}H_{12}O_3$ 204.0786, found 204.0785.

trans-*2-Chloro-5-hydroxy-4-methoxy-2-cyclopenten-1-one* (**2g**). The ring contraction of pyranone **1g**[5] (163 mg, 1 mmol) in DMF (30 mL) with NaHCO$_3$ (420 mg, 5 mmol), nBu$_4$N$^+$Cl$^-$ (277 mg, 1 mmol) and Pd(OAc)$_2$ (20 mg, 0.09 mmol) (80°C, 24 h) gave cyclopentenone **2g** (42 mg, 26%) as colorless crystals, mp 102 -104°C. IR (KBr) ν 3340, 2980, 2940, 1735, 1600, 1390, 1280, 1220, 1190, 1110, 960 cm^{-1}; 200 MHz ^{1}H NMR (CD_2Cl_2) δ 7.44 (d, $J_{3,4}$

= 2 Hz, 1 H, H-3), 4.34 (dd, $J_{3,4}$ = 2 Hz, $J_{4,5}$ = 2 Hz, 1 H, H-4), 4.25 (d, $J_{4,5}$ = 2 Hz, 1 H, H-5), 3.55 (s, OCH_3), 3.09 (bs, 1 H, OH); *m/z* 163/162 (M^+, 10/32), 132/131 (34/100), 102 (42), 75 (16), 69 (18), 50 (23).

trans-*2-Bromo-5-hydroxy-4-methoxy-2-cyclopenten-1-one* (**2h**). The reaction of pyranone **1h**[5] (207 mg, 1 mmol) in DMF (30 mL) with $NaHCO_3$ (420 mg, 5 mmol), $nBu_4N^+Cl^-$ (277 mg, 1 mmol) and $Pd(OAc)_2$ (20 mg, 0.09 mmol) (80°C, 24 h) afforded cyclpentenone **2h** (50 mg, 24%, colorless crystals, mp 114 -116°C). IR (KBr) *ν* 3340, 2980, 1940, 1735, 1590, 1400, 1340, 1280, 1220, 1190, 1110, 960 cm^{-1}; 80 MHz ^1H NMR (DMSO-d_6) δ 8.02 (d, $J_{3,4}$ = 2.5 Hz, 1 H, H-3), 6.15 (d, $J_{5,OH}$ = 6.5 Hz, 1 H, OH), 4.27 (dd, $J_{3,4}$ = 2.5 Hz, $J_{4,5}$ = 2 Hz, 1 H, H-4), 4.12 (dd, $J_{5,OH}$ = 6.5 Hz, $J_{4,5}$ = 2 Hz, 1 H, H-5), 3.44 (s, 3 H, OCH_3); *m/z* 208/206 (M^+, 7), 207/205 (62), 177/175 (42), 176/174 (100), 147/145 (52), 137 (49), 101 (73).

trans-*5-Hydroxy-4-methoxy-3-methyl-2-cyclopenten-1-one* (**2i**). Ring contraction of methylpyranone **1i** (41 mg, 0.288 mmol) in DMF (6.1 mL) in the presence of $NaHCO_3$ (121 mg, 1.44 mmol), $Et_3N^+CH_2Ph\ Cl^-$ (66 mg, 0.289 mmol) and $Pd(OAc)_2$ (1.3 mg, 5.79 μmol) (80°C, 35 h) gave starting material **1i** (8 mg, 20%) and cyclopentenone **2i** (12.5 mg, 30%, oil). IR ($CHCl_3$) *ν* 3550, 3420, 3000, 2940, 2835, 1705, 1620, 1431, 1376, 1311, 1116, 1092, 978, 911, 830 cm^{-1}; 200 MHz ^1H NMR δ 6.01 (quintet, ^4J = 1.25 Hz, 1 H, H-2), 4.23 - 4.16 (m, 2 H, H-4 and H-5), 3.61 (s, 3 H, OCH_3), 3.23 (bs, 1 H, OH), 2.15 (t, ^4J = 1.25 Hz, 3 H, CH_3); *m/z* 142 (M^+, 42), 127 (M^+-CH_3, 50), 114 (M^+-CO, 19), 111 (M^+-OCH_3, 56), 110 (25), 82 (100), 55 (80). Exact mass calcd for $C_7H_{10}O_3$ 142.0630, found 142.0630.

trans-*5-Hydroxy-3-isopropyl-4-methoxy-2-cyclopenten-1-one* (**2j**). Reaction of isopropylpyranone **1j** (35 mg, 0.206 mmol) in DMF (4.3 mL) with $NaHCO_3$ (86 mg, 1.03 mmol) and $Et_3N^+CH_2Ph\ Cl^-$ (46 mg, 0.205 mmol) (80°C, 37 h) gave, in order of elution, cyclopentenone **2j** (3.5 mg, 10%), alcohol **4** (4.5 mg, 12%) and alcohol **3** (3.6 mg, 9%) as oils. Data of **2j**: IR ($CHCl_3$) *ν* 3550, 3420, 2971, 2935, 2877, 2833, 1713, 1607, 1467, 1186, 1117, 1090, 978 cm^{-1}; 200 MHz ^1H NMR δ 5.99 (t, ^4J = 1.1 Hz, 1 H, H-2), 4.28 (bd, $J_{4,5}$ = 2.5 Hz, 1 H, H-5), 4.22 (d, $J_{4,5}$ = 2.5 Hz, 1 H, H-4), 3.60 (s, 3 H, OCH_3), 2.82 (b septet, ^3J= 6.5 Hz, 1 H, $(CH_3)_2CH$), 1.60 (bs, 1 H, OH), 1.20 (d, ^3J= 6.5 Hz, 3 H, CH_3), 1.16 (d, ^3J= 6.5 Hz, 3 H, CH_3); *m/z* 170 (M^+, 30), 139 (M^+-CH_3O, 24), 138 (M^+-CH_4O, 18), 127 (M^+-C_3H_7, 100), 95 (63), 81 (33), 67 (44). Exact mass calcd for $C_9H_{14}O_3$ 170.0943, found 170.0944. Data of **4**: IR (cap film) *ν* 3340, 2987, 2916, 2835, 1715, 1371, 1244, 1198, 1098, 1069, 960 cm^{-1}; 200 MHz ^1H NMR δ 5.15 (s, 1 H, H-6), 4.22 (d, ^2J = 17.5 Hz, 1 H, H-2), 4.07 (d, ^2J = 17.5 Hz, 1 H, H-2), 3.64 (s, 1 H, H-4), 3.51 (s, 3 H, OCH_3), 2.23 (bs, 1 H, OH), 1.34 (s, 3 H, CH_3), 1.33 (s, 3 H, CH_3). Data of **3**: IR (cap film) *ν* 3450, 2980, 2935,

2835, 1685, 1636, 1366, 1268, 1184, 1119, 1062, 963 cm^{-1}; 200 MHz ^1H NMR δ 6.07 (s, 1 H, H-4), 5.28 (s, 1 H, H-6), 4.37 (d, ^2J = 16.8 Hz, 1 H, H-2), 4.07 (d, ^2J = 16.8 Hz, 1 H, H-2), 3.54 (s, 3 H, OCH_3), 2.06 (bs, 1 H, OH), 1.46 (s, 3 H, CH_3), 1.43 (s, 3 H, CH_3); 50.3 MHz ^{13}C NMR δ 195.51 (s, C-3), 164.56 (s, C-5), 121.12 (d, C-4), 94.54 (d, C-6), 71.29 (t, C-2), 64.76 (s, $(CH_3)_2COH$), 56.42 (q, OCH_3), 29.49 (q, CH_3), 29.08 (q, CH_3); *m/z* 186 (M^+, 5.6), 171 (M^+-CH_3, 1.9), 156 (M^+-CH_2O, 71), 155 (M^+-CH_3O, 27), 139 (27), 124 (100), 109 (43), 96 (37), 81 (40), 67 (58), 59 (32).

(+)-R-4-(2-Trimethylsilylethoxy)-2-cyclopenten-1-one. A solution of $CrCl_2$ (Aldrich, ~90%, 450 mg, ~3.3 mmol) in degassed water (3 mL) under argon was added by syringe to a stirred solution of diastereomerically pure camphanate **9-A**[13] (168 mg, 0.426 mmol) in degassed redistilled acetone (6 mL) under argon. After 12 h the reaction mixture was extracted with ether (3x) and the combined organic layers were washed with brine, dried ($MgSO_4$) and evaporated *in vacuo* at 0°C. Column chromatography of the residue on silica gel (7 g, ether/petrol, 4 : 6) afforded the title compound as a colorless liquid (65 mg, 77%), $[\alpha]_D^{25}$ = +49.7°, $[\alpha]_{578}^{25}$ = +50.4°, $[\alpha]_{546}^{25}$ = +51.0°, $[\alpha]_{436}^{25}$ = -26.6° (c = 1.37, CH_2Cl_2). IR (cap film) ν 3066, 2954, 2895, 2864, 1724, 1656, 1591, 1348, 1249, 1181, 1109, 1073, 858, 837 cm^{-1}; 200 MHz ^1H NMR δ 7.59 (dd, $J_{2,3}$ = 5.8 Hz, $J_{3,4}$= 2.3 Hz, 1 H, H-3), 6.22 (dd, $J_{2,3}$ = 5.8 Hz, $J_{2,4}$ = 1.2 Hz, 1 H, H-2), 4.64 (m, 1 H, H-4), 3.60 (m, 2 H, $OCH_2CH_2SiMe_3$), 2.66 (dd, ^2J = 18 Hz, $J_{4,5}$= 6 Hz, 1 H, H-5), 2.26 (dd, ^2J = 18 Hz, $J_{4,5}$= 2.2 Hz, 1 H, H-5), 0.93 (m, 2 H, $OCH_2CH_2SiMe_3$), 0.0 (s, 9 H, Me_3Si); 50.3 MHz ^{13}C NMR δ 206.10 (s, C-1), 161.31 (d, C-3), 135.37 (d, C-2), 76.84 (d, C-4), 67.09 (t, $OCH_2CH_2SiMe_3$), 41.74 (t, C-5), 18.39 (t, $OCH_2CH_2SiMe_3$), -1.43 (q, Me_3Si); *m/z* 198 (M^+, 1.5), 183 (M^+-CH_3, 3.2), 168 (6.5), 155 (94), 142 (6.2), 103 (17.5), 81 (76), 75 (42), 73 (100).

(+)-R-4-Hydroxy-2-cyclopenten-1-one **(+)-10.** $ZnCl_2 \cdot OEt_2$ (0.1 mL of a 2.2 M solution in CH_2Cl_2, 0.22 mmol) was added to a stirred solution of (+)-R-4-(2-trimethylsilylethoxy)-2-cyclopenten-1-one (38 mg, 0.19 mmol) in CH_2Cl_2 (0.9 mL) under N_2. After 16 h sat. aq. $NaHCO_3$ solution (0.2 mL) was added and the mixture extracted with ethyl acetate (4 x 2 mL). The combined extracts were dried ($MgSO_4$) and concentrated *in vacuo*. Purification of the residue by column chromatography on silica gel (3 g, ether) afforded cyclopentenone **(+)-10** as an oil. Traces of water were removed by dissolving the product in $CHCl_3$ (1 mL), drying (Na_2SO_4) and evaporating *in vacuo* to yield the prostaglandin building block **(+)-10** (17 mg, 90%), physical data identical to the literature,[12] including optical rotations:[12c] $[\alpha]_D^{22}$ = +94.2° ± 2.8°, $[\alpha]_{578}^{22}$ = +95.5° ± 2.9°, $[\alpha]_{546}^{22}$ = +97.6° ± 2.9°, $[\alpha]_{436}^{22}$ = -22.4° ± 0.9° (c = 0.74, MeOH).

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