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NEW METHODS FOR REDUCTIVE FREE-RADICAL CYCLIZATIONS OF α-BROMOACETALS TO 2-ALKOXYTETRAHYDROFURANS WITH ACTIVATED CHROMIUM(II)-ACETATE

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Abstract: A method for the synthesis of γ-butyrolactones **6** is described in which the key step is a free-radical cyclization of α-bromoacetals **4** to 2-alkoxytetrahydrofurans **5** in 54-93% yield induced by activated chromium(II)-acetate. Four new methods have been developed in order to activate the transition metal. Two of them require only catalytic amounts of chromium(II)-acetate, because it can be regenerated *in situ* chemically or electrochemically. The diastereoselectivity of the cyclization depends on the substitution pattern of **4** and ranges between 30.4:1 and 1:54.8.

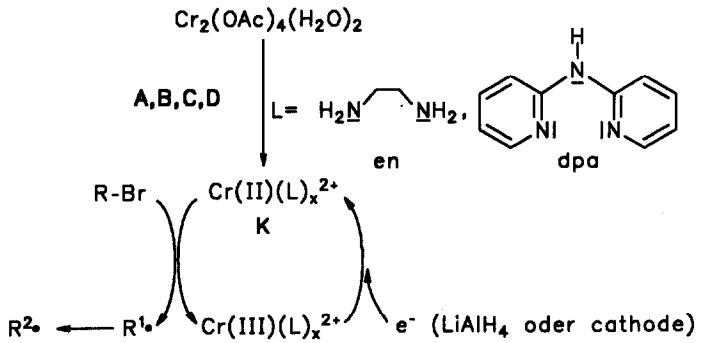
Introduction

Free-radical cyclizations have become an important method for constructing five and six membered ring skeletons.[1] The radicals are obtained from halides with Bu_3SnH,[2] $(CH_3Si)_3SiH$[3] or cobalt complexes,[4] from alkenes by acetoxymercuration and $NaBH_4$-reduction,[5] by hydrogen abstraction[6] from tertiary carbon atoms, by manganese(III) oxidation of enolizable compounds,[7] by reduction of carbonyl compounds[8] or by *Kolbe*-electrolysis of carboxylates.[9] The most commonly used Bu_3SnH, however, has the drawback to be toxic and difficult to separate from the products unless it is immobilized.[2c]

The radical cyclization of reactive $\Delta^{5,6}$-unsaturated α-bromo- or α-iodoesters induced by chromium(II)-acetate is an efficient, new and convenient method.[10] In contrast to cyclizations by Bu_3SnH the products are easily obtained metal free because of the high water solubility of the formed chromium(III)-complexes.

Results

We now found that alkylbromides being less reactive than α-bromoesters can be reduced to radicals in aqueous THF by $Cr_2(OAc)_4(H_2O)_2$ in the presence of the ligands ethylenediamine (en) (method **A**) or 2,2'-dipyridylamine (dpa) (method **B**). In the first case the reducing agent seems to be $[Cr(II)(en)_2]^{2+}$(**1**).[11] The structure of the second complex is unknown. It is also possible to regenerate **1** chemically with $LiAlH_4$ (method **C**) or electrochemically (method **D**) (Scheme 1).



A: 1.50 equiv. $Cr_2(OAc)_4(H_2O)_2$ / 12 equiv. en /THF/H_2O (2:1).
B: 1.50 equiv. $Cr_2(OAc)_4(H_2O)_2$ / 12 equiv. dpa /THF/H_2O (2:1).
C: 0.30 equiv. $Cr_2(OAc)_4(H_2O)_2$ / 2.6 equiv. en /*abs.* THF/ 8 equiv. $LiAlH_4$.
D: 0.15 equiv. $Cr_2(OAc)_4(H_2O)_2$ / 33 equiv. en /0.2 m $LiClO_4$, DMF/glassy carbon cathode, -1.15 V *vs. Marple*-electrode.[12]

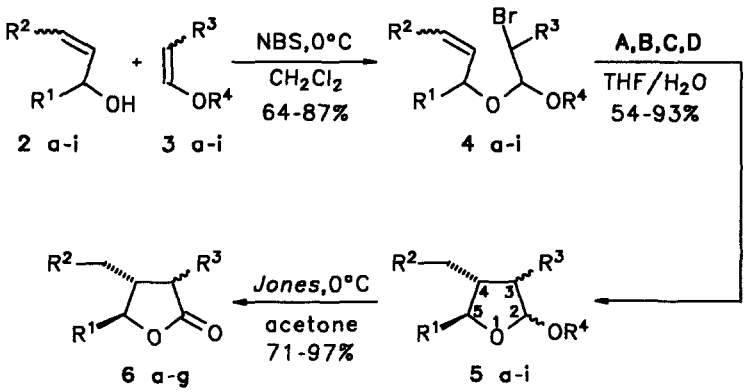
Scheme 1.

The α-bromoacetals **4** react in aqueous THF at room temperature with the *in situ* prepared activated chromium(II)-complexes to tetrahydrofurans **5** in good to excellent yields (Scheme 2, Table 2). The 2-alkoxy-1-bromoacetals **4** are obtained by bromo-alkoxidation of vinylethers **3** with allylic or homoallylic alcohols **2** and *N*-bromosuccinimide (NBS) as bromine donor (Scheme 2, Table 1). In order to synthesize the naturally occurring, pleasant smelling[13] 4-butanolides: 4,5-dihydro-4-methyl-2(3*H*)-furanone (**6a**), a flavor of soybeans and tobacco,[14] 4,5-dihydro-4,5-dimethyl-2(3*H*)-furanone (**6b**), a component in soybean lecithin[15], *whisky* lactone (*quercus* lactone A)(**6c**)[16] and *cognac* lactone (**6d**),[17] and to determine the diastereoselectivity at C-3, C-4, respectively at C-4, C-5 the mixed acetals **5** are converted into γ-butyrolactones **6** by *Jones* oxidation[18] in excellent yields (Table 3). The stereochemistry of **5h** and **6d,f** was established by ^1H NMR-NOE measurements, those of **5a,i** and **6 b,c,e,g** were determined by comparing their chemical shifts in ^1H NMR with literature data and their retention times in GLC with those of **5h** and **6d,f**.

The reaction is believed to proceed by a free-radical mechanism and presumably involves alkyl free radicals **i** and **k** as intermediates[11]. It is assumed that the reductive cleavage of the C-Br bond in **4** by Cr(II) leads to **i** (Scheme 3), which undergoes intramolecular cyclization to **k**. This is trapped by Cr(II) to afford the organochromium species **l**, which is subsequently hydrolyzed to **5**. If the trapping occurs prior to cyclization, **m** is formed, which hydrolizes to the acyclic hydrogenation product.

The 5-*exo-trig* cyclization of the intermediate radical **i** is favoured against its trapping by an other equivalent of chromium(II) by a high cyclization rate ($k_c > 3*10^7\ s^{-1}$)[13] and a low active chromium(II)-concentration. This concentration seems to be low in all methods. In the two phase system of method **A** $[Cr(II)(en)_2]^{2+}$**(1)** has a very low solubility in the organic phase. In method **B** the

complex between $Cr_2(OAc)_4(H_2O)_2$ and 2,2'-dipyridylamine (dpa) is only slightly soluble in aqueous THF. In methods **C** and **D** additionally substoichiometric amounts of $Cr_2(OAc)_4(H_2O)_2$ are used. The solvolysis of the organochromium-complexes **l** and **m** are accelerated by OAc^--ions.[11f] Acyclic products have never been observed under these conditions.



Scheme 2.

Table 1: *Synthesis of acetals* **4**

entry	2 R^1	2 R^2	3 R^3	3 R^4	Yield (%) 4
a	H	H	H	C_4H_9	78
b	CH_3	H	H	C_2H_5	78
c	C_4H_9	H	H	C_2H_5	87
d	C_5H_{11}	H	H	C_2H_5	85
e	H	H	CH_3	C_2H_5	64
f	H	H	C_4H_9	C_2H_5	73
g	$-(CH_2)_3-$		H	C_2H_5	81
h	H	H	$-(CH_2)_2-$		80
i	H	H	$-(CH_2)_3-$		71
j	$HC{\equiv}CCH_2OH$		H	C_2H_5	65

Table 2: Synthesis of tetrahydrofurans **5**

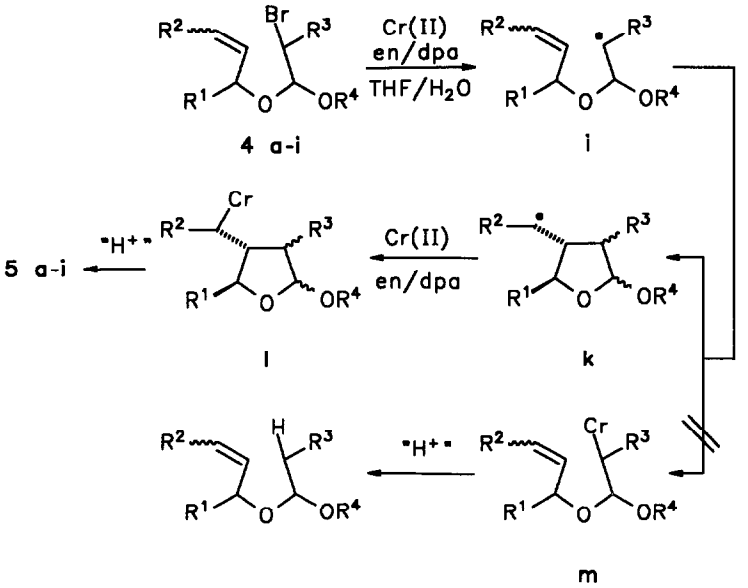
4	R^1	R^2	R^3	R^4	Yield (%) 5 A	B	C	D	Isomers[a]	*trans/cis*[b]
a	H	H	H	C_4H_9	75	81	/	/	2t:2c	**A**:6.5:1[c]
b	CH_3	H	H	C_2H_5	66	67	71	77	4 Isomers[d]	**A**:12.5:1
										B:13.7:1
										C:12.6:1
										D:11.6:1
c	C_4H_9	H	H	C_2H_5	84	88	93	70	4 Isomers[d]	**A**:29.2:1
										B:30.4:1
										C:29.3:1
										D:26.7:1
d	C_5H_{11}	H	H	C_2H_5	89	86	75	84	4 Isomers[d]	**A**:29.2:1
										B:30.4:1
										C:29.3:1
										D:24.4:1
e	H	H	CH_3	C_2H_5	54	75	/	/	3 Isomers[d]	**A**:1:1.51
										B:1:1.86
f	H	H	C_4H_9	C_2H_5	76	90	83	67	4 Isomers[d]	**A**:1:1.16[e]
										B:1:1.47
										C:1:1.30[f]
										D:1:1.23
g	$-(CH_2)_3-$		H	C_2H_5	75	70	83	75	2t5c:2c5c	**A-D**: 1:1
h	H	H	$-(CH_2)_2-$		87	75	85	70[g]	2t3t:2c3c	**A**:1:28.3
										B:1:28.9
										C:1:18.6
										D:1:54.8
i	H	H	$-(CH_2)_3-$		80	71	89	80	2t3t:2c3c	**A**:1:8.4[h]
										B:1:9.2
										C:1:5.2
										D:1:15.8
j	$HC{\equiv}CCH_2-$		H	C_2H_5	81	/	/	/	/	/

a) For assignment of the configuration the 4-alkylgroup serves as a reference substituent; b) Determined by GLC-integration; c) Estimated by ^1H NMR (300 MHz) analysis; d) The selectivity refers to the configuration of C-4 to C-5 or C-3 to C-4; e) *Trans/cis*-selectivity in water = 1.19 : 1; f) *Trans/cis*-selectivity with three equivalents Cr(II) without $LiAlH_4$ = 1 : 1.36; g) Configuration determined by ^1H NMR-NOE analysis; h) *Trans/cis*-selectivity in *abs.* DMF = 1 : 17.6.

Table 3: Synthesis of γ-butyrolactones **6**

5	Yield (%) 6	Isomers[a]	*trans/cis*[b]			
a	93	/	/			
b	86	4r5t:4r5c	**A**: 12.5:1,	**B**: 13.7:1,	**C**: 12.6:1,	**D**: 11.6:1
c	91	4r5t:4r5c	**A**: 29.2:1,	**B**: 30.4:1,	**C**: 29.3:1,	**D**: 26.7:1
d	97	4r5t:4r5c	**A**: 29.2:1,	**B**: 30.4:1,	**C**: 29.3:1,	**D**: 24.4:1
e	85	3t4r:3c4r	**A**: 1:1.51,	**B**: 1:1.86		
f	97	3t4r:3c4r	**A**: 1:1.16,	**B**: 1:1.47,	**C**: 1:1.30,	**D**: 1:1.23
g	71	4r5t:4r5c	**A-D:**	>1:98		

a)For assignment of the configuration the 4-alkyl group serves as a reference substituent;
b) Determined by GLC-integration.

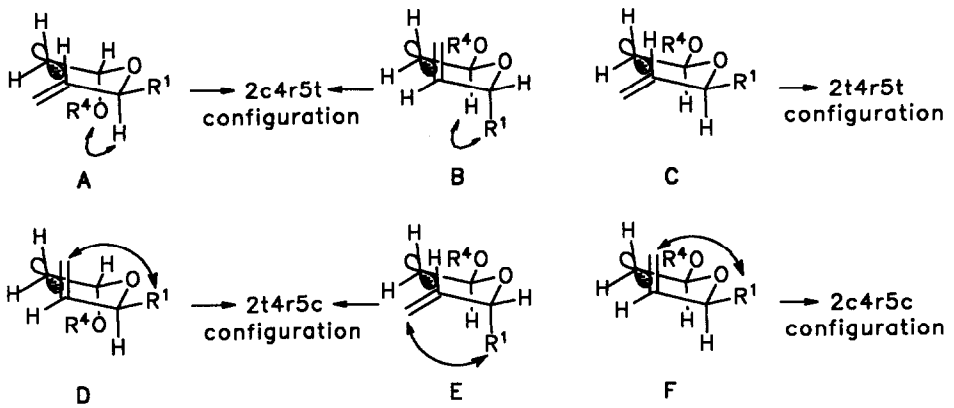


Scheme 3.

The results show that the diastereoselectivity of the 5-*exo-trig* cyclizations varies with the Cr(II) ligand and the solvent.

In the cyclizations of **4** to **5** a less stabilized radical[20] reacts with the double bond. Therefore one can suppose a relative early transition state with a large distance of about 227 pm[19] between the radical and the double bond. Thus the relative energies of transition states resembling the configuration of **I** (Scheme 3) determine the diastereoselectivity.

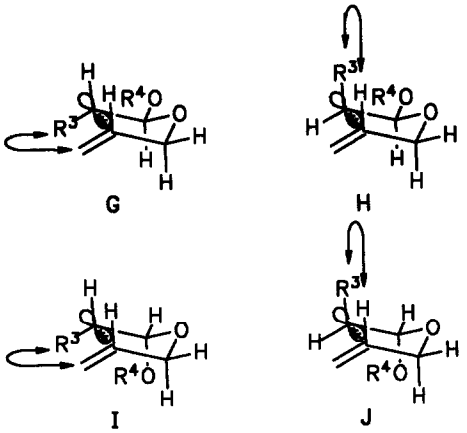
Using the *Beckwith-Houk* model[19] the high stereoselectivity of the radical cyclization to **5 b-d** is due to the 5-substituent R^1. In the diastereomeric transition states **A**, **B** and **C** the double bond is forced *trans* to R^1. This *trans*-selectivity is also reported by other authors.[10,21] This steric repulsion is apparently more pronounced than the the pseudoaxial interaction of the ethoxy group or R^1 with the axial hydrogen in the transition states **A** and **B** (Scheme 4). In the transition state **C** all substituents are arranged in the energetically favorable pseudoequatorial position. It leads to the 2t,5t-diastereomer. In method **D** the *trans*-selectivity decreases. This indicates a stronger solvation of the oxygen in DMF as compared to the reaction in THF, whereby the size of oxygen is increased, which leads to a stronger steric interaction between OR^4 and the double bond and thus causes a higher preference of transition state **D**.



Scheme 4: Transition states **A** - **F** leading to **5a-d**

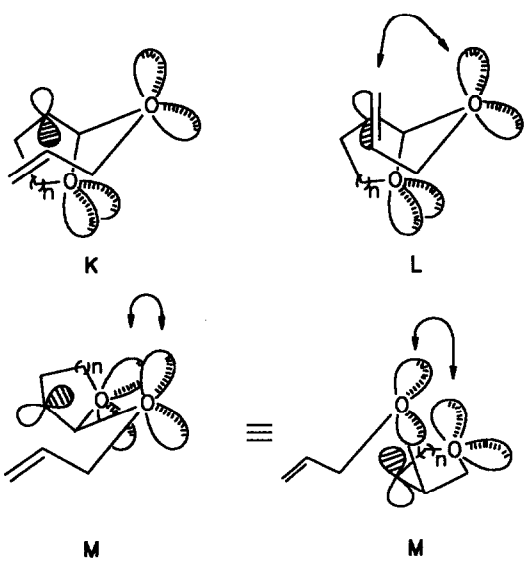
In the cyclizations to **5e** and **5f** and their subsequent oxidation to **6e,f** (Table 3) the well documented moderate *cis*-selectivity[19] between the C-3 and the C-4 substituent was seen. The same results have been found for the reaction of **4h** and **4i**. In particular the cyclization of **4h** produces a 54.8:1 (method **D**) ratio of *endo*-**5h** to *exo*-**5h**. This *cis*(*endo*)-selectivity is a general phenomena for intramolecular radical additions leading to carbocycles. Electron-withdrawing, radical stabilising groups, however, lead to a *trans*-selectivity.[10,22]

Using the *Beckwith-Houk* model for different substituted radicals four chair- and four boat-like transition states can be drawn for the cyclization to the monocyclic compounds **5e** and **f**. Among these we may assume that the four chair-like conformers **G**, **H**, **I** and **J** have the lower energy (Scheme 5).



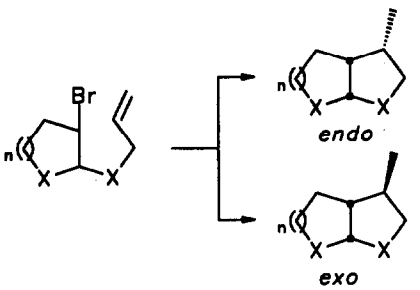
Scheme 5: Transition states **G** - **J** leading to **5e-f**

In transition state **G** and **I** R^3 occupies an energetically favourable *pseudo*-equatorial position, while in **H** and **J** it is *pseudo*-axial. The major product from substrates with a small substituent ($R^3 = CH_3$) therefore results from **G** and **I** leading to the *cis*-3,4-disubstituted tetrahydrofurans. In the case of a bulkier substituent ($R^3 = C_4H_9$) the steric interaction with the double bond is larger. The *cis*-selectivity decreases somewhat because more radicals cyclize *via* the transition states **H** and **J**. For the reaction leading to the bicyclic tetrahydrofurans three transition states **K**, **L** and **M** can be assumed (Scheme 6).



Scheme 6: Transition states **K** - **M** leading to bicyclic tetrahydrofurans **5h-i**

The high *endo*-selectivity appears to be caused by the conformation of the five- or six-membered ring which forces the single occupied orbital of the radical in **M** to be twisted away from the orientation of a most favourable interaction with the p-orbitals of the double bond, whilst the p-Π-overlap seems to be strain free in **K** and **L**. The reason for the higher selectivity in our case compared with this leading to carbocyclic rings[23] (Table 4, Scheme 7) is probably due to the interaction of the free electron pairs at oxygen in the transition state **M**, which additionally disfavours this conformer. The quite recently discussed boat form[21] **L** also seems to be energetically unfavorable, because of the interaction between the double bond and the free electron pair at oxygen.[20] The solvent effect in method **D**, which increases the steric demand of the oxygen, additionally disfavours **M** and **L** and rises the selectivity.



	x	n
5h	O	1
5i	O	2
7a	CH_2	1
7b	CH_2	2

Scheme 7.

Table 4: *Endo/exo*-selectivity in the cyclization to **5h,i** and **7a,b**

	endo/exo-selectivity (method: Bu_3SnH/C_6H_6)[23]		*endo/exo*-selectivity (method: **A,B,C,D**)
7a	8.3:1	**5h**	**A**: 28.3:1 **B**: 28.9:1 **C**: 18.6:1 **D**: 54.8:1
7b	3.5:1	**5i**	**A**: 8.4:1 **B**: 9.2:1 **C**: 5.2:1 **D**: 15.8:1

Conclusion

α-Bromoacetals are converted by a radical cyclization to 2-alkoxytetrahydrofurans in 54-93% yield. The tetrahydrofurans can be oxidized in 71-97% yield to γ-butyrolactones. The cyclization is initiated by Cr(II), which is activated by an amine ligand, whereby also less reactive organohalides can be transformed. Cr(II) can also be used in substoichiometric amounts by regeneration with $LiAlH_4$ or at the cathode. Depending on the position and size of the alkyl groups in the α-bromoacetal high *trans*- or *cis(endo)*-selectivities are obtained, these depend in some cases strongly on the solvent.

EXPERIMENTAL

General: ^{1}H-NMR spectra were taken on a *Bruker* WM 300 spectrometer in $CDCl_3$. IR-spectra were recorded on a *Shimadzu*-IR408 or a *Nicolet* 5 DXC-FT-IR. Mass spectra were taken on a *Finnigan*-MAT CH-8230+datasystem *Finnigan*-MAT SS 300 or an ion trap mass spectrometer *Varian-Saturn* II. Flash column chromatography was performed with *Merck* silica gel 60 (230-400) mesh. For electrolysis was used a divided glass cell, a *Metrohm*-glassy carbon cathode EA602, a platinum anode, Cd/Hg reference electrode (*Marple*-electrode)[12] and a *Wenking*-ST88 potentiostat.

General procedure: Preparation of α-bromoacetals **4**.
1.96 g (11 mmol) *N*-bromosuccinimide is added slowly to a stirred solution of 10 mmol vinyl ether and 20 mmol allylalcohol at 0 °C in 200 ml CH_2Cl_2. After 6 h the solvent is removed by distillation and the residue separated by column chromatography (eluent: petrolether/ether (PE/Et_2O)).

1-Bromo-2-butoxy-2-(1-propene-3-oxy)ethane[10d] (**4a**). Yield: 1.85 g (7.8 mmol, 78 %).

IR (Film): $\tilde{\nu}$ = 3075 cm^{-1}, 2975, 2920, 1455, 1420, 1040, 990, 920.
MS (70eV): *m/z* (%) = 179/181 (7/5) [M^+ -C_3H_5O], 163/165 (4/5) [M^+ -C_4H_9O], 162/164 (7/5) [M^+ -C_4H_9OH], 143 (3) [M^+ -CH_2Br], 121/123 (8/11), 87 (13), 57 (36), 41 (100).
^{1}H-NMR ($CDCl_3$): δ = 5.97-5.86 [m, 1H, C*H*=], 5.34-5.18 [m, 2H, =CH_2], 4.71 [t, *J* = 5.5 Hz, 1H, C*H*$(OR)_2$], 4.19-4.04 [m, 2H, 2-OCH_2CH=CH_2], 3.66-3.47 [m, 2H, OC$H_2(CH_2)_2CH_3$], 3.38 [d, *J* = 5.5 Hz, 2H, CH_2Br], 1.63-1.54 [m, 2H, $OCH_2CH_2CH_2CH_3$], 1.46-1.34 [m, 2H, $O(CH_2)_2CH_2CH_3$], 0.93 [t, *J* = 7.3 Hz, 3H, butyl-CH_3].

1-Bromo-2-ethoxy-2-(1-butene-3-oxy)ethane (**4b**). Yield: 1.74 g (7.8 mmol, 78 %).

IR (Film): $\tilde{\nu}$ = 3075 cm^{-1}, 2978, 2930, 1422, 1372, 1109, 1059, 1024, 994.
MS (70eV): *m/z* (%) = 207/209 (1/1) [M^+ -CH_3], 177/179 (1/1) [M^+ -C_2H_5O], 151/153 (24/24) [M^+ -C_4H_7O], 123/125 (27/26) [M^+ -C_4H_7O -C_2H_4], 75 (54), 55 (100).
^{1}H-NMR ($CDCl_3$): δ = 5.87-5.67 [m, 1H, C*H*=], 5.25-5.14 [m, 2H, =CH_2], 4.73-4.67 [m, 1H, C*H*$(OR)_2$], 4.21-4.09 [m, 1H, OC*H*(Me)CH=CH_2], 3.73-3.52 [m, 2H, OCH_2CH_3], 3.38-3.33 [m, 2H, CH_2Br], 1.42-1.18 [m, 6H, OCH_2CH_3 and $OCH(CH_3)CH=CH_2$].
(Found: C, 42.90, H, 6.73, $C_8H_{15}BrO_2$ requires C, 43.06, H, 6.78 %).

1-Bromo-2-ethoxy-2-(1-heptene-3-oxy)ethane (**4c**). Yield: 2.29 g (8.7 mmol, 87 %).

IR (Film): $\tilde{\nu}$ = 3079 cm^{-1}, 2959, 2932, 1113, 1056, 1026, 994.
MS (70eV): *m/z* (%) = 207/209 (2/2) [M^+ -C_4H_9], 151/153 (60/59) [M^+ -$C_7H_{13}O$], 123/125 (27/27) [M^+ -$C_7H_{13}O$ -C_2H_4], 97 (62) [$C_7H_{13}^+$], 55 (100).
^{1}H-NMR ($CDCl_3$): δ = 5.81-5.61[m, 1H, C*H*=], 5.23-5.12 [m, 2H, =CH_2], 4.72-4.65 [m, 1H, C*H*$(OR)_2$], 4.01-3.87 [m, 1H, OC*H*(C_4H_9)CH=CH_2], 3.72-3.45 [m, 2H, OCH_2CH_3], 3.38-3.12 [m, 2H, CH_2Br], 1.65-1.22 [m, 9H, OCH_2CH_3 and butyl-CH_2], 0.92-0.87 [m, 3H, butyl-CH_3].

(Found: C, 50.05, H, 8.15, $C_{11}H_{21}BrO_2$ requires C, 49.82, H, 7.98 %).

1-Bromo-2-ethoxy-2-(1-octene-3-oxy)ethane (**4d**). Yield: 1.37 g (8.5 mmol, 85 %).

IR (Film): $\tilde{\nu}$ = 3083 cm^{-1}, 2976, 2957, 2932, 1422, 1114, 1057, 1026, 994.
MS (70eV): *m/z* (%) = 207/209 (34/33) [M^+ -C_5H_{11}], 151/153 (100/99) [M^+ -$C_8H_{15}O$], 123/125 (44/43) [M^+ -$C_8H_{15}O$ -C_2H_4], 111 (31) [$C_8H_{15}^+$], 69 (46).
^{1}H-NMR ($CDCl_3$): δ = 5.88-5.63 [m, 1H, C*H*=], 5.23-5.14 [m, 2H, =CH_2], 4.70-4.67 [m, 1H, C*H*$(OR)_2$], 4.05-3.85 [m, 1H, OC*H*(C_5H_{11})CH=CH_2], 3.70-3.45 [m, 2H, OCH_2CH_3], 3.37-3.33 [m, 2H, CH_2Br], 1.69-1.17 [m, 11H, OCH_2CH_3 and pentyl-CH_2], 0.94-0.86 [m, 3H, pentyl-CH_3].
(Found: C, 51.52, H, 8.22, $C_{12}H_{23}BrO_2$ requires C, 51.62, H, 8.30 %).

2-Bromo-1-ethoxy-1-(1-propene-3-oxy)propane (**4e**). Yield: 1.43 g (6.4 mmol, 64 %).

IR (Film): $\tilde{\nu}$ = 3082 cm^{-1}, 2979, 2874, 1377, 1112, 1054, 927.
MS (70eV): *m/z* (%) = 177/179 (1/1) [M^+ -C_2H_5O], 165/167 (4/3) [M^+ -C_3H_5O], 137/139 (5/5) [M^+ -C_3H_5O,-CO], 115 (28) [$C_3H_5OCHOCH_2CH_3^+$], 57 (24) [$C_3H_5O^+$], 41 (100).
^{1}H-NMR ($CDCl_3$): δ = (main diastereomer) 5.94-5.88 [m, 1H, C*H*=], 5.35-5.18 [m, 2H, =CH_2], 4.53 [t, *J* = 5.5 Hz, 1H, C*H*$(OR)_2$], 4.13-4.00 [m, 3H, C*H*Br and OCH_2CH=CH_2], 3.75-3.60 [m, 2H, OCH_2CH_3], 1.67 [m, 3H, CHBrCH_3Br], 1.24 [t, *J* = 6.9 Hz, 3H, OCH_2CH_3].
(Found: C, 42.82, H, 6.78, $C_8H_{15}BrO_2$ requires C, 43.06, H, 6.78 %).

2-Bromo-1-ethoxy-1-(1-propene-3-oxy)hexane (**4f**). Yield: 1.93 g (7.3 mmol, 73 %).

IR (Film): $\tilde{\nu}$ = 3060 cm^{-1}, 2975, 2870, 2820, 1440, 1365, 1090, 1030, 910.
MS (70eV): *m/z* (%) = 219/221 (3/2) [M^+ -C_2H_5O], 207/209 (6/7) [M^+ -C_3H_5O], 177/179 (2/2), 115 (100) [$C_3H_5OCHOCH_2CH_3^+$], 81 (11), 69 (10), 57 (10), 41 (48).
^{1}H-NMR ($CDCl_3$): δ = 5.98-5.89 [m, 1H, C*H*=], 5.35-5.18 [m, 2H, =CH_2], 4.58 [t, *J* = 5.4 Hz, 1H, C*H*$(OR)_2$], 4.18-4.01 [m, 2H, OCH_2CH=CH_2], 3.99-3.95 [m, 1H, C*H*Br], 3.75-3.61 [m, 2H, OCH_2CH_3], 2.01-1.16 [m, 9H, OCH_2CH_3 and butyl-CH_2], 0.94-0.85 [m, 3H, butyl-CH_3].
(Found: C, 49.99, H, 7.82, $C_{11}H_{21}BrO_2$ requires C, 49.82, H, 7.98 %).

1-Bromo-2-ethoxy-2-(1-cyclohexene-3-oxy)ethane[2a] (**4g**). Yield: 2.02 g (81 mmol, 81 %).

IR (Film): $\tilde{\nu}$ = 3050 cm^{-1}, 2995, 2950, 2900, 1420, 1345, 1110, 1050.
MS (70eV): *m/z* (%) = 203/205 (1/1) [M^+ -C_2H_5O], 151/153 (48/47) [M^+ -C_6H_9O], 123/125 (42/42) [M^+ -C_6H_9O -C_2H_4], 98 (15) [$C_6H_9O^+$], 81 (100) [C_6H_9O], 72 (32)
^{1}H-NMR ($CDCl_3$): δ = 5.95-5.65 [m, 2H, C*H*=C*H*], 4.80-4.63 [m, 1H, C*H*$(OR)_2$], 4.20-4.10 [m, 1H, OC*H*$(CH_2)_3$CH=CH-], 3.67-3.50 [m, 2H, OCH_2CH_3], 3.42-3.34 [m, 2H, CH_2Br], 1.69-1.17 [m, 9H, OCH_2CH_3 and cyclo-CH_2.].

3-Bromo-2-allyloxytetrahydrofuran (**4h**). Yield: 1.64 g (8.0 mmol, 80 %).

IR (Film): $\tilde{\nu}$ = 3081 cm^{-1}, 3041, 2982, 2898, 1437, 1118, 1069, 1028, 922.
MS (70eV): *m/z* (%) = 205/207 (1/1) [M^+ -H], 165/167 (4/3) [M^+ -C_3H_5], 149/151 (37/37) [M^+ -C_3H_5O], 119/121 (8/8) [M^+ -C_3H_5O-CH_2O], 99 (34) [M^+ -C_2H_4Br], 56 (35), 41 (100).
^{1}H-NMR ($CDCl_3$): δ = (main diastereomer) 5.93-5.84 [m, 1H, C*H*=], 5.30-5.10 [m, 3H, =CH_2 and 2-H], 4.25-3.99 [m, 5H, 5-CH_2, CHBr and OCH_2CH=CH_2], 2.96-2.61 and 2.25-2.18 [m, 2H, 4-CH_2].
(Found: C, 40.83, H, 5.45, $C_7H_{11}BrO_2$ requires C, 40.61, H, 5.35 %).

3-Bromo-2-allyloxytetrahydropyran (**4i**).[21b] Yield: 1.56 g (7.1 mmol, 71 %).

IR (Film): $\tilde{\nu}$ = 3081 cm^{-1}, 2950, , 2854, 1434, 1392, 1130, 1073, 1030, 924.

MS (70eV): *m/z* (%) = 220/222 (1/1) [M^+], 219/221 (1/1) [M^+ -H], 179/181 (5/5) [M^+ -C_3H_5], 163/165 (55/55) [M^+ -C_3H_5O], 133/351 (35/35) [M^+ -C_3H_5O -CH_2O], 99 (52), 55 (100), 41 (90).
^{1}H-NMR ($CDCl_3$): δ = (main diastereomer) 5.94-5.88 [m, 1H, C*H*=], 5.35-5.19 [m, 2H, =C*H*$_2$], 4.66 [d, *J* = 4.4 Hz, 1H, 2-H], 4.29-3.88 [m, 4H, 6-C*H*$_2$, and OC*H*$_2$CH=CH$_2$], 3.61-3.46 [m, 1H, C*H*Br], 2.43-2.36, 1.98-1.89 and 1.55-1.52 [m, 4H, 4-C*H*$_2$ and 5-C*H*$_2$].

1-Bromo-2-ethoxy-2-(1-propyne-3-oxy-)ethane (**4j**). Yield: 1.35 g (6.5 mmol, 65 %).

IR (Film): $\tilde{\nu}$ = 3310 cm^{-1}, 2995, 2885, 1435, 1380, 1120, 1050, 720.
MS (70eV): *m/z* (%) = 205/207 (1/1) [M^+ -H], 161/163 (4/4) [M^+ -C_2H_5O], 151/153 (6/6) [M^+ -C_3H_3O], 121/123 (4/3) [M^+ -C_3H_3O -CO], 113 (100) [$C_3H_3OCHOCH_2CH_3^+$], 39 (100) [$C_3H_3^+$].
^{1}H-NMR ($CDCl_3$): δ = 4.88-4.85 [m, 1H, 2-H], 4.14 [d, *J* = 4.6 Hz, 2H, OC*H*$_2$C≡CH]. 3.77-3.59 [m, 2H, OC*H*$_2$CH$_3$], 3.42 [d, *J* = 3.2 Hz, 2H, C*H*$_2$Br], 2.46 [t, ^{4}*J* = 2.3 Hz, 1H, ≡C*H*], 1.25 [t, *J* = 6.9 Hz, 3H, OCH$_2$C*H*$_3$].
(Found: C, 40.79, H, 5.30, $C_7H_{11}BrO_2$ requires C, 40.61, H, 5.35 %).

Preparation of tetrahydrofurans 5.[26]
Method **A:** To a stirred solution of 3 mmol bromoacetal **4** in 40 ml degassed aqueous THF(THF:H_2O = 2:1, v/v) was added under nitrogen first 1.7 g (9 mmol) $Cr_2(OAc)_4(H_2O)_2$ and then 2.2 g (36 mmol) ethylendiamine (en). The solution was stirred for 12 h at 20 °C, then 10 ml water was added and the mixture is extracted with ether. The organic phase was dried ($MgSO_4$) and evaporated. The product was purified by column chromatography (eluent: PE/Et_2O).

Method **B:** To a stirred solution of 3 mmol bromoacetal **4** in 40 ml degassed aqueous THF(THF:H_2O = 2:1, v/v) was added under nitrogen first 1.7 g (9 mmol) $Cr_2(OAc)_4(H_2O)_2$ and then 6.1 g (36 mmol) 2,2'-dipyridylamine (dpa). The solution was stirred for 6 h at 20 °C, then 10 ml 2N HCl was added to the pink precipitate and the mixture was extracted with ether. The organic phase was dried ($MgSO_4$) and evaporated. The product was purified by column chromatography (eluent: PE:Et_2O > 5:1).

Method **C:** To a stirred solution of 1 mmol bromoacetal **4** in 20 ml degassed *abs.* THF was added under nitrogen first 0.125 g (0.33mmol) $Cr_2(OAc)_4(H_2O)_2$ and 2.2 g (36 mmol) ethylenediamine (en) and then over 40 min 0.304 g (8 mmol) $LiAlH_4$ in little portions at 15 °C. The solution was stirred for 1 h at rt, then 20 ml ice and 10 ml brine were added and the mixture was extracted with ether. The organic phase was dried ($MgSO_4$) and evaporated. The product was purified by column chromatography (eluent: PE/Et_2O).

Method **D:** To 20 ml of a stirred, degassed and dry electrolyte (0.2 m $LiClO_4$ in DMF) in a jacketed glass cell was added under nitrogen first 0.054 g (0.15mmol) $Cr_2(OAc)_4(H_2O)_2$ and then 2.0 g (33 mmol) ethylendiamine (en). Afterwards 1 mmol bromoacetal **4** is added at 20 °C. Then the electroysis was carried out potentiostatically at -1.15 V *vs. Marple*-electrode at glassy carbon. After 600-800 As the solution was quenched with 10 ml brine and the mixture is extracted with PE:Et_2O = 3:1. The organic phase was dried ($MgSO_4$) and evaporated. The product was purified by column chromatography (eluent: PE:Et_2O = 5:1).

3-Butoxy-4-methyl-tetrahydrofuran (**5a**).[21b] Yield: 0.355 g (2.25 mmol, 75 %).

IR (Film): $\tilde{\nu}$ = 2960 cm^{-1}, 2930, 2906, 2880, 1455, 1377, 1115, 1085, 920.
MS (70eV): *m/z* (%) = 158 (1) [M^+], 157 (1) [M^+ -H], 101 (5) [M^+ -C_4H_9], 85 (100) [M^+ -C_4H_9O], 47 (44), 41 (66).

^{1}H-NMR ($CDCl_3$): δ = (main diastereomer) 5.10 [dd, *J* = 5.1, 3.0 Hz, 1H, 2-H], 3.92 [dd, *J* = 7.8, 7.7 Hz, 1H, 5-H], 3.67 [d, *J* = 9.4, 6.8, 6.7 Hz, 1H, 2-C*H*HC$_3$H$_7$], 3.44-3.33 [m, 2H, 2-OCH*H*C$_3$H$_7$ and 5-H], 2.28-2.22 [m, 2H, 3-CH_2], 1.59-1.33 [m, 5H 4-H and 2-CH$_2$(CH_2)$_2$CH$_3$], 1.07 [d, *J* = 6.4 Hz, 3H, 4-CH_3], 0.91 [t, *J* = 7.3 Hz, 3H, butyl-CH_3].

2-Ethoxy-4,5-dimethyl-tetrahydrofuran (**5b**). Yield: 0.285 g (1.98 mmol, 66 %).

IR (Film): $\tilde{\nu}$ = 2945 cm^{-1}, 2890, 1435, 1365, 1085, 1050, 895, 720.
MS (70eV): *m/z* (%) = 144 (1) [M$^+$], 143 (3) [M$^+$ -H], 129 (3) [M$^+$ -CH$_3$], 115 (2), 100 (65), 99 (76) [M$^+$ -C$_2$H$_5$O], 85 (61), 70 (84), 57 (79), 55 (100) 43 (65).
^{1}H-NMR ($CDCl_3$): δ = 5.11-5.00 [m, 1H, 2-H], 3.79-3.71 [m, 2H, 2-OCH_2CH$_3$], 3.70-3.40 [m, 1H, 5-H], 2.40-1.40 [m, 3H, 4-H and 3-CH_2], 1.29-1.16 [m, 6H, 5-CH_3 and OCH_2CH$_3$], 1.03-1.00 [m, 3H, 4-CH_3].
(Found: C, 66.71, H, 11.22, $C_8H_{16}O_2$ requires C, 66.63, H, 11.18 %).

5-Butyl-2-ethoxy-4-methyl-tetrahydrofuran (**5c**). Yield: 0.468 g (2.52 mmol, 84 %).

IR (Film): $\tilde{\nu}$ = 2959 cm^{-1}, 2931, 2906, 1445, 1377, 1109, 1089, 996.
MS (70eV): *m/z* (%) = 185 (2) [M$^+$ -H], 141 (18) [M$^+$ -C$_2$H$_5$O], 129 (48) [M$^+$ -C$_4$H$_9$], 101 (62) [M$^+$ -C$_4$H$_9$ -CO], 100 (89) [M$^+$ -C$_5$H$_{10}$O], 85 (77), 57 (86) [C$_4$H$_9^+$], 55(100).
^{1}H-NMR ($CDCl_3$): δ = 5.12-5.00 [m, 1H, 2-H], 3.76-3.71 [m, 1H, 5-H], 3.50-3.39 [m, 2H, 2-OCH_2CH$_3$], 2.40-2.03 [m, 7H, 4-H and butyl-CH$_2$], 1.22-1.16 [m, 3H, OCH$_2$CH_3], 1.05-1.01 [m, 3H, 4-CH_3], 0.93-0.89 [m, 3H, butyl-CH_3].
(Found: C, 70.94, H, 11.95, $C_{11}H_{22}O_2$ requires C, 70.72, H, 11.90 %).

2-Ethoxy-4-methyl-5-pentyl-tetrahydrofuran (**5d**). Yield: 0.534 g (2.67 mmol, 89 %).

IR (Film): $\tilde{\nu}$ = 2958 cm^{-1}, 2931, 2873, 1458, 1373, 1109, 1075, 995.
MS (70eV): *m/z* (%) = 200 (1) [M$^+$], 199 (3) [M$^+$-H], 155 (26) [M$^+$ -C$_2$H$_5$O], 129 (82) [M$^+$ -C$_5$H$_{11}$], 101 (69) [M$^+$ -C$_5$H$_{11}$ -CO], 100 (100) [M$^+$ -C$_6$H$_{13}$O], 85 (55), 71 (32) [C$_5$H$_{11}^+$], 55 (31).
^{1}H-NMR ($CDCl_3$): δ = 5.10-5.00 [m, 1H, 2-H], 3.80-3.71 [m, 1H, 5-H], 3.53-3.36 [m, 2H, 2-OCH_2CH$_3$], 2.34-2.01 [m, 2H, 3-H], 1.58-1.31 [m, 9H, 4-H and pentyl-CH$_2$], 1.23-1.16 [m, 3H, OCH$_2$CH_3], 1.05-1.01 [m, 3H, 4-CH_3], 0.92-0.87 [m, 3H, pentyl-CH_3].
(Found: C, 72.18, H, 12.17, $C_{12}H_{24}O_2$ requires C, 71.95, H, 12.08 %).

2-Ethoxy-3,4-dimethyl-tetrahydrofuran (**5e**). Yield: 0.235 g (1.63 mmol, 54 %).

IR (Film): $\tilde{\nu}$ = 2945 cm^{-1}, 2900, 2850, 1445, 1360, 1090, 995.
MS (70eV): *m/z* (%) = 143 (2) [M$^+$ -H], 114 (8) [M$^+$ -CH$_2$O], 99 (55) [M$^+$ -C$_2$H$_5$O], 71 (34), 70 (100) [M$^+$ -C$_2$H$_5$OH -CO], 55 (71), 41(26).
^{1}H-NMR ($CDCl_3$): δ = 4.90-4.68 [m, 1H, 2-H], 4.10-3.65 [m, 2H, 5-H], 3.60-3.40 [m, 2H, 2-OCH_2CH$_3$], 2.60-1.40 [m, 2H, 3-H and 4-H], 1.20-1.00 [m, 9H, OCH_2CH$_3$, 3-CH_3 and 4-CH_3].
(Found: C, 66.58, H, 11.14, $C_8H_{16}O_2$ requires C, 66.63, H, 11.18 %).

3-Butyl-2-ethoxy-4-methyl-tetrahydrofuran (**5f**). Yield: 0.424 g (2.28 mmol, 76 %).

IR (Film): $\tilde{\nu}$ = 2940 cm^{-1}, 2895, 2840, 1448, 1365, 1090, 1005, 930.
MS (70eV): *m/z* (%) = 185 (2) [M$^+$ -H], 156 (2) [M$^+$ -CH$_2$O], 141 (100) [M$^+$ -C$_2$H$_5$O], 123 (15), 112 (71) [M$^+$ -C$_2$H$_5$OH -CO], 99 (27), 83 (82), 70 (87), 55 (79), 41 (55).
^{1}H-NMR ($CDCl_3$): δ = 4.90-4.74 [m, 1H, 2-H], 4.06-3.58 [m, 2H, 5-H], 3.50-3.35 [m, 2H, 2-OCH_2CH$_3$], 2.45-1.38 [m, 2H, 3-H and 4-H], 1.32-1.24 [m, 6H, butyl-CH_2], 1.23-0.88 [m, 9H, OCH_2CH$_3$, 3-butyl-CH_3 and 4-CH_3].

(Found: C, 70.92, H, 12.17, $C_{11}H_{22}O_2$ requires C, 70.92, H, 11.90 %).

2-Ethoxy-(3ar,7ac)octahydro[b]furan (**5g**). Yield: 0.383 g (2.25 mmol, 75 %).

IR (Film): $\tilde{\nu}$ = 2974 cm^{-1}, 2932, 2864, 1447, 1346, 1118, 1104, 998.
MS (70eV): *m/z* (%) = 170 (8) [M^+], 169 (4) [M^+ -H], 140 (8) [M^+ -CH_2O], 125 (30) [M^+ -C_2H_5O], 170 (14), 96 (92) [M^+ -C_2H_5OH -CO], 81 (100), 67 (42), 41 (24).
^{1}H-NMR ($CDCl_3$): δ = 5.20-5.20 [m, 1H, 2-H], 4.20-3.90 [m, 1H, 7a-H], 3.85-3.40 [m, 2H, 2-OC*H*$_2$CH$_3$], 2.10-1.30 [m, 11H], 1.21 [t, *J* = 7.0 Hz, 3H, OCH_2CH_3].
(Found: C, 70.72, H, 10.71, $C_{10}H_{18}O_2$ requires C, 70.55, H, 10.66 %).

endo-4-Methyl-2,8-dioxabicyclo[3.3.0]octane (**5h**). Yield: 0.334 g (2.61 mmol, 87 %).

IR (Film): $\tilde{\nu}$ = 2961 cm^{-1}, 2875, 1456, 1369, 1037, 1005, 922.
MS (70eV): *m/z* (%) = 128 (2) [M^+], 127 (2) [M^+ -H], 98 (100) [M^+ -CH_2O], 83 (65) [M^+ -C_2H_5O], 69 (31) [M^+ -C_3H_7O], 55 (17), 41 (46).
^{1}H-NMR ($CDCl_3$): δ = 5.71 [d, *J* = 4.9 Hz, 1H, 1-H], 3.93-3.83 [m, 3H, $3H_{exo}$, 7-C*H*$_2$], 3.36 [dd, *J* = 11.2, 8.4 Hz, 1H, $3\text{-}H_{endo}$], 2.75 [dddd, *J* = 8.0, 4.9, 4.7, 4.6 Hz, 1H, 5-H], 2.41 [ddqd, *J* = 11.2, 8.0, 6.9, 4.1 Hz, 1H, 4-H], 1.93-1.75 [m, 2H, 6-C*H*$_2$], 1.12 [d, *J* = 6.9 Hz, 3H, 4-C*H*$_3$].
^{1}H-NMR-NOE ($CDCl_3$): irradiation in the resonance of 1-H raises the intensity of the signals from 5-H (4%) and 4-H (1%); in 5-H raises 1-H (7%) and 4-H (3%); in 4-C*H*$_3$ raises $3H_{endo}$ (3%) and 6-C*H*$_2$ (3%).
(Found: C, 65.84, H, 9.69, $C_7H_{12}O_2$ requires C, 65.60, H, 9.43 %).

endo-7-Methyl-2,9-dioxabicyclo[4.3.0]nonane (**5i**).[24] Yield: 0.341 g (2.40 mmol, 80 %).

IR (Film): $\tilde{\nu}$ = 2936 cm^{-1}, 2877, 1454, 1381, 1145, 1065, 1019, 922.
MS (70eV): *m/z* (%) = 142 (17) [M^+], 141 (100) [M^+ -H], 127 (1) [M^+ -CH_3], 112 (27) [M^+ -CH_2O], 97 (45) [M^+ -C_2H_5O], 84 (31), [M^+ -C_3H_7O], 81 (48), 69 (38), 55 (38), 41 (27).
^{1}H-NMR ($CDCl_3$): δ = 5.28 [d, *J* = 3.9 Hz, 1H, 1-H], 3.97-3.58 [m, 4H, 3-C*H*$_2$, 8-C*H*$_2$], 2.47-2.41 [m, 1H, 6-H], 1.93-1.88 [m 1H, 7-H], 1.67-1.37 [m, 4H, 4-C*H*$_2$ and 5-C*H*$_2$], 0.98 [d, *J* = 6.9 Hz, 3H, 7-C*H*$_3$].

2-Ethoxy-4-methylene-tetrahydrofuran (**5j**). Yield: 0.311 g (2.43 mmol, 81 %).

IR (Film): $\tilde{\nu}$ = 3040 cm^{-1}, 2975, 2850, 1448, 1370, 1350, 1100, 925.
MS (70eV): *m/z* (%) = 128 (48) [M^+], 127 (4) [M^+ -H], 100 (7) [M^+ -CO], 99 (17), 83 (61) [M^+ -C_2H_5O], 72 (45) [M^+ -C_3H_4O], 55 (24), 43 (100).
^{1}H-NMR ($CDCl_3$): δ = 5.21 [t, *J* = 5.1 Hz, 1H, 2-H], 5.02-4.96 [m, 2H, =C*H*$_2$], 4.38-4.34 [m, 2H, 5-C*H*$_2$], 3.77-3.45 [m 2H, OC*H*$_2$CH$_3$], 2.74-2.45 [m, 2H, 3-C*H*$_2$], 1.21 [d, *J* = 5.2 Hz, 3H, OCH_2CH_3].
(Found: C, 65.57, H, 9.54, $C_7H_{12}O_2$ requires C, 65.60, H, 9.43 %).

Preparation of γ-butyrolactones 6.
4.4 ml *Jones*-reagent[18] is added within 1 h to an ice cooled solution of 1 mmol tetrahydrofuran **5** in 5 ml acetone. After further 15 min, excess of isopropylalcohol is added. The resulting suspension is poured into 50 ml water by decantation and the residual greenish precipitates are washed with 25 ml acetone four times. The combined aqueous solutions are neutralized with conc. aqueous $NaHCO_3$ (pH = 7.5) and then extracted with $CHCl_3$. The extract is dried with $MgSO_4$ and evaporated.

4,5-Dihydro-4-methyl-2-(3*H*)-furanone (**6a**)[10d]. Yield: 0.093 g (0.93 mmol, 93 %).

IR (Film): $\tilde{\nu}$ = 2969 cm^{-1}, 2931, 1782, 1458, 1420, 1173, 1018, 996.

MS (70eV): *m/z* (%) = 100 (10) [M^+], 70 (5) [M^+ -CH_2O], 56 (42) [M^+ -CO_2], 42 (100) [M^+ -$C_2H_2O_2$], 41 (62) [$C_3H_5^+$].
^{1}H-NMR ($CDCl_3$): δ = 4.41 [dd, *J* = 8.8, 7.2 Hz, 1H, 5-H], 3.87 [dd, *J* = 8.8 Hz, *J* = 6.3 Hz, 1H, 5-H], 2.70-2.10 [m, 3H, 4-H, 3-C*H*$_2$], 1.16 [d, *J* = 6.3 Hz, 3H, 4-C*H*$_3$].

trans-4,5-Dihydro-4,5-dimethyl-2-(3*H*)-furanone (**6b**)[15a-c]. Yield: 98 mg (0.86 mmol, 86 %).

IR (Film): $\tilde{\nu}$ = 2974 cm^{-1}, 2934, 2863, 1779, 1455, 1296, 1180, 1058, 1037, 932.
MS (70eV): *m/z* (%) = 114 (3) [M^+], 113 (2) [M^+ -H], 99 (14) [M^+ -CH_3], 86 (1) [M^+ -CO], 71 (23) [M^+ -CH_3 -CO], 70 (45) [M^+ -CO_2], 55 (34), 45 (62), 42 (100), 41 (35).
^{1}H-NMR ($CDCl_3$): δ = 4.14 [dq, *J* = 7.6, 6.3 Hz, 1H, 5-H], 2.80-2.62 and 2.25-2.09 [m, 3H, 4-H and 3-C*H*$_2$]. 1.40 [d, *J* = 6.3 Hz, 3H, 5-C*H*$_3$], 1.14 [t, *J* = 6.3 Hz, 3H, 4-C*H*$_3$].
(Found: C, 62.92, H, 9.04, $C_6H_{10}O_2$ requires C, 63.14, H, 8.83 %).

trans-Whisky lactone (**6c**)[16a]. Yield: 1.42 g (0.91 mmol, 91 %).

IR (Film): $\tilde{\nu}$ = 2960 cm^{-1}, 2863, 1781, 1458, 1211, 1171, 1124, 1037, 932.
MS (70eV): *m/z* (%) = 156 (1) [M^+], 128 (2) [M^+ -CO], 114 (3) [M^+ -C_3H_6], 99 (100) [M^+ -C_4H_9], 71 (42), 43 (43).
^{1}H-NMR ($CDCl_3$): δ = 4.00 [dt, *J* = 7.7, 4.0 Hz, 1H, 5-H], 2.72-2.61 and 2.24-2.14 [m, 3H, 4-H and 3-C*H*$_2$], 1.80-1.20 [m, 6H, butyl-C*H*$_2$], 1.13 [d, *J* = 6.3 Hz, 3H, 4-C*H*$_3$], 0.91 [t, *J* = 7.3 Hz, 3H, butyl-C*H*$_3$].
(Found: C, 69.34, H, 10.28, $C_9H_{16}O_2$ requires C, 69.19, H, 10.23 %).

trans-Cognac lactone (**6d**). Yield: 0.166 g (0.97 mmol, 97 %).

IR (Film): $\tilde{\nu}$ = 2959 cm^{-1}, 2933, 1780, 1460, 1209, 1170, 1126, 1072, 938.
MS (70eV): *m/z* (%) = 170 (1) [M^+], 142 (4) [M^+ -CO], 128 (8) [M^+ -C_3H_6], 114 (8), 110 (10), 99 (100) [M^+ -C_5H_{11}], 71 (47), 43 (26).
^{1}H-NMR ($CDCl_3$): δ = 4.00 [dt, *J* = 7.6, 4.1 Hz, 1H, 5-H], 2.64 [dd, *J* = 9.0, 8.6 Hz, 1H, 3-H*trans* to 4-Me], 2.24-2.16 [m, 2H, 4-H and 3-H*cis* to 4-Me], 1.78-1.23 [m, 8H, pentyl-C*H*$_2$], 1.13 [d, *J* = 6.4 Hz, 3H, 4-C*H*$_3$], 0.90 [t, *J* = 6.6 Hz, 3H, pentyl-C*H*$_3$].
^{1}H-NMR-NOE ($CDCl_3$): irradiation in the resonance of 5-H raises the intensity of the signal from 4-C*H*$_3$ (3%); in 4-C*H*$_3$ raises 5-H (11%).
(Found: C, 69.34, H, 10.28, $C_{10}H_{18}O_2$ requires C, 69.19, H, 10.23 %).

3,4-Dimethyltetrahydrofuran-2-one (**6e**). Yield: 0.098 g (0.85 mmol, 85 %).

IR (Film): $\tilde{\nu}$ = 2950 cm^{-1}, 2900, 1765, 1445, 1375, 1170, 1124, 1000, 970.
MS (70eV): *m/z* (%) = 114 (15) [M^+], 70 (45) [M^+ -CO_2], 56 (47) [M^+ -C_3H_6O], 55 (100), 42 (45), 41 (35).
^{1}H-NMR ($CDCl_3$): δ = *cis*-lactone[27] 4.29 [dd, *J* = 8.8, 5.8 Hz, 1H, 5-H], 3.94 [dd, *J* = 8.2, 3.2 Hz, 1H, 5-H], 2.70-2.58 [m, 2H, 4-H and 3-H], 1.15 [d, *J* = 6.1 Hz, 3H, 3-C*H*$_3$], 1.05 [d, *J* = 6.9 Hz, 3H, 4-C*H*$_3$].
^{1}H-NMR ($CDCl_3$): δ = *trans*-lactone 4.46-4.30 [m, 1H, 5-H], 3.70 [dd, *J* = 9.4, 9.4 Hz, 1H, 5-H], 2.70-2.58 [m, 1H, 4-H], 2.21-2.05 [m, 1H, 3-H], 1.24 [d, *J* = 6.8 Hz, 3H, 4-C*H*$_3$], 1.13 [d, *J* = 6.9 Hz, 3H, 4-C*H*$_3$].
(Found: C, 63.02, H, 9.07, $C_6H_{10}O_2$ requires C, 63.14, H, 8.83 %).

3-Butyl-4-methyltetrahydrofuran-2-one (**6f**). Yield: 0.142 g (0.97 mmol, 97 %).

IR (Film): $\tilde{\nu}$ = 2980 cm^{-1}, 2950, 1775, 1460, 1380, 1170, 1115, 985.

MS (70eV): *m/z* (%) = 156 (1) [M^+], 141 (3) [M^+ -CH_3], 113 (10) [M^+ -CH_3 -CO], 100 (75), 85 (100), 59 (17), 55 (23), 41 (26).
^{1}H-NMR ($CDCl_3$): δ = *cis*-lactone 4.26 [dd, *J* = 8.9, 5.45 Hz, 1H, 5-H], 3.96 [dd, *J* = 8.9, 1.9 Hz, 1H, 5-H], 2.70-2.48 [m, 2H, 4-H and 3-H], 1.77-1.32 [m, 6H, butyl-CH_2], 1.02 [d, *J* = 6.9 Hz, 3H, 4-CH_3], 0.91 [t, *J* = 6.6 Hz, 3H, butyl-CH_3].
^{1}H-NMR-NOE ($CDCl_3$): irradiation in the resonance of butyl-CH_2 raise the intensity of the signal from 4-CH_3 (1%).
^{1}H-NMR ($CDCl_3$): *trans*-lactone 4.36 [dd, *J* = 8.8, 7.5 Hz, 1H, 5-H], 3.72 [dd, *J* = 8.8, 8.8 Hz, 1H, 5-H], 2.37-2.32 [m, 1H, 4-H], 2.13-2.06 [m, 1H, 3-H], 1.73-1.25 [m, 6H, butyl-CH_2] 1.15 [d, *J* = 6.6 Hz, 3H, 4-CH_3], 0.90 [d, *J* = 6.7 Hz, 3H, butyl-CH_3].
^{1}H-NMR-NOE ($CDCl_3$): irradiation in the resonance of 3-H raise the intensity of the signal from 4-CH_3 (1%); in butyl-CH_3 raise 4-H (2%).
(Found: C, 69.38, H, 10.36, $C_9H_{16}O_2$ requires C, 69.19, H, 10.32 %).

cis-Hexahydro-2(3*H*)-benzofuran (**6g**)[25]. Yield: 99.4 mg (0.71 mmol, 71 %).

IR (Film): $\tilde{\nu}$ = 2934 cm^{-1}, 2859, 1776, 1448, 1423, 1173, 1141, 942.
MS (ion trap): *m/z* (%) = 141 (45) [M^+ +H], 140 (3) [M^+], 139 (2) [M^+ -H], 111 (4), 95 (16), 81 (100), 67 (24), 55 (26), 39 (57).
^{1}H-NMR ($CDCl_3$): δ = 4.52 [m, 1H, OC*H*], 2.65-1.00 [m, 11H].
(Found: C, 68.392, H, 8.65, $C_8H_{12}O_2$ requires C, 68.55, H, 8.63 %).

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