Tetrahedron Vol 47, No 37, pp 7875-7886, 1991
Printed in Great Britain

0040-4020/91 $3 00+ 00

Reactivity of *in situ* Generated Dihalomethyllithium towards Dicarboxylic Acid Diesters and Lactones: Synthetic Applications

José Barluenga,*[a] Luján Llavona,[a] Miguel Yus,[b] and José M Concellón[a]

[a] Departamento de Química Organometálica, Universidad de Oviedo, E-33071 Oviedo, Spain

[b] Departamento de Química Orgánica, Universidad de Alicante, E-03690 Alicante, Spain

(*Received in UK 27 June* 1991)

Abstract. *The reaction of dicarboxylic acid diesters* **1**, *with in situ generated dihalomethyllithium (1 1 4 molar ratio) at -78°C leads, after hydrolysis, to the corresponding dihalomethylketoesters* **3** *The same process using an excess of the carbenoid (1 4 molar ratio) yields the expected tetrahalodiketones* **5** *The reaction of these carbenoids with γ- and δ-lactones* **6** *at -78 °C yields, after hydrolysis, 2-(dihalomethyl) γ- or δ-lactols* **7** *or* **8**, *respectively The reaction of lactols* **7** *or* **8** *with trimethylsilane or allyltrimethylsilane in the presence of BF_3OEt_2 affords the corresponding substituted tetrahydrofurans or pyrans* **10** *or* **12** *The use of ε-caprolactone as starting material in the reaction with dihalomethyllithium leads to the corresponding 1,1-dihalo-7-hydroxy-2-heptanones*

INTRODUCTION

The reaction of only one ester group of dicarboxylic acid diesters has proven to be a valuable synthetic strategy for the preparation of many natural products [1] So, the preparation of half-esters by selective enzymatic hydrolysis of dicarboxylic acid diesters has received much attention [2] The addition of organolithium compounds to only one of both carbonyl groups of dicarboxylic acids diesters, it has not been reported in the literature [3] A similar transformation can be carried out using dicarboxylic acids derivatives with carbonyl groups of different reactivity,[4] such as chlorocarbonylesters or using cyclic anhydrides [5] On the other hand, tetrahydropyrans and tetrahydrofurans are common structural elements in terpenoids, pheromones, antibiotics, C-glycosides and other biologically active natural products [1,6] For this reason their synthesis has received much attention during the last decade [7] Recently we have described the synthesis of α,α-dihaloketones[8] or α,α,α'-trihaloketones[9] from *in situ* generated dihalomethyllithium[10] and carboxylic or α-halocarboxylic acids esters, respectively In the

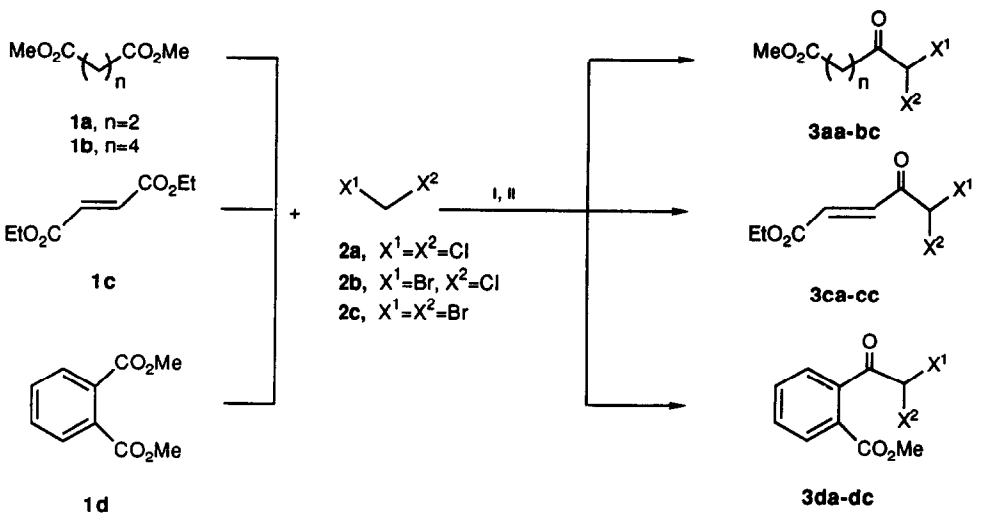
+Dedicated to the memory of Prof F Gaviña

present paper we describe a simple, easy and rapid method for the preparation of dihalomethylketoesters by reaction of 1 equivalent of dihalomethyllithium generated *in situ* with dicarboxylic acid diesters The synthesis and reactivity of 2-(dihalomethyl)-2-hydroxytetrahydrofurans (γ-lactols) and pyrans (δ-lactols) starting from *in situ*-generated dihalomethyllithium and γ- or δ-lactones, respectively is also described here.

RESULTS AND DISCUSSION

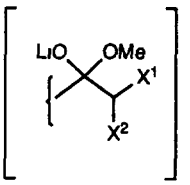
a) Reaction of dihalocarbenoids with dicarboxylic acid diesters

The successive treatment of several commercially available dicarboxylic acid diesters **1** with dichloromethane (**2a**), bromochloromethane (**2b**), or dibromomethane (**2c**) (1 1 4 molar ratio) and then with lithium dialkylamide (1.1 6 molar ratio) at -78°C led, after acid hydrolysis, to the corresponding dihalomethylketoesters **3** (Scheme 1 and Table 1)



Scheme 1 Reagents I, R_2NLi, II, HCl / H_2O

It is noteworthy that under these reaction conditions, the dihalogenated ketoester **3** was contaminated only with small amounts (<10%) of the starting diester **1** The isolation of the pure ketoester **3** was achieved easily by column chromatography on silica gel The reaction times were short (about 0 5 h) and the lithiation reaction was carried out with lithium diisopropylamide for dibromomethane (**2c**) or chlorobromomethane (**2b**) and with lithium dicyclohexylamide for dichloromethane (**2a**)[8] In general, the transformation of the ester function into ketone can be explained since the intermediate of the type **4** is stable under the reaction conditions due to the presence of electronegative halogen substituents,[11] and so the addition of two molecules of dihalomethyllithium to the ester group is not possible When the reaction was carried out with an excess of dihalomethyllithium the corresponding tetrahalogenated diketones **5** were obtained (Scheme 2 and Table 2) The generation of the corresponding carbenoids from **2a-c** was done as described above

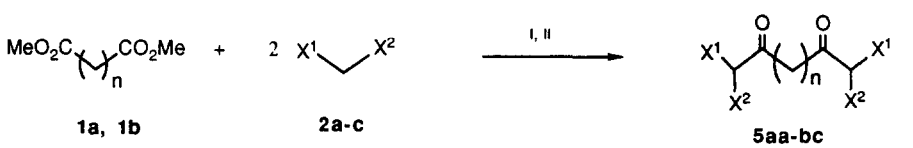


4aa-4dc

Table 1 Synthesis of Dihaloketoesters 3

Diester	Dihalomethane	Product 3		
		no	Yield,[a]%	R_f
1a	**2a**	**3aa**	65 (59)	0 37[b]
1b	**2a**	**3ba**	58 (52)	0 45[b]
1c	**2a**	**3ca**	67 (60)	0 42[c]
1c	**2b**	**3cb**	53 (45)	0 32[c]
1c	**2c**	**3cc**	76 (70)[d]	0 40[e]
1d	**2a**	**3da**	70 (62)	0 35[e]
1d	**2b**	**3db**	72 (63)	0 45[f]
1d	**2c**	**3dc**	77 (74)	0 42[f]

[a] Yield of crude product based on starting material 1, yield of isolated produt after column cromatography on silica gel (hexane-ether) is given in parenthesis [b] Hexane/ether 3/2 [c] Hexane/ether 9/1 [d] Dichloromethane/hexane 7/3 [e] Hexane/ether 4/1 [f] Hexane/ether 1/1



1a, 1b **2a-c** **5aa-bc**

Scheme 2 Reagents I, $2R_2NLi$, II, HCl / H_2O

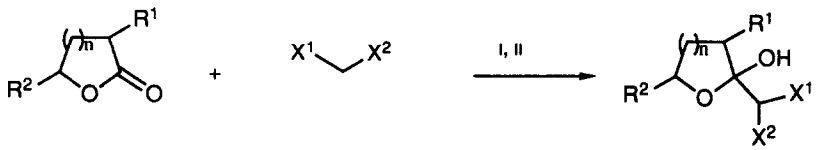
2 Synthesis of Tetrahaloketones **5**

ester	Dihalomethane	Product **5** no	Yield,[a]%	mp(°C)
a	**2a**	**5aa**	72 (65)	47-48
b	**2a**	**5ba**	68 (60)	51-52
b	**2b**	**5bb**	62 (52)	69-70
b	**2c**	**5bc**	64 (57)	77-78

ield of crude product based on starting material **1**, yield of isolated product after recrystallization (hexane) is given in nesis

action of Dihalocarbenoids with lactones

The successive treatment of different γ- and δ-lactones **6** with dichloromethane (**2a**), ochloromethane (**2b**) or dibromomethane (**2c**) (1 2 molar ratio) and lithiumdiisopropylamide (1 2 ratio) at -78 °C afforded 2-(dihalomethyl)-2-hydroxytetrahydrofurans or pyrans **7** or **8**, ctively (Scheme 3 and Table 3) When it is possible a mixture of diastereoisomers was isolated



6a, $R^1=R^2=H$, n=1
6b, $R^1=Br$, $R^2=H$, n=1
6c, $R^1=H$, $R^2=CH_3$, n=1
6d, $R^1=R^2=H$, n=2

2a-c

7aa-cc, n=1
8da-dc, n=2

Scheme 3 Reagents I, Pr_2^iNLi, II, HCl / H_2O

The addition of dihalomethyllithium to the lactone takes place in a short time (ca 20 min) and no etition with the ring opening to give the corresponding ketoalcohol (see below) was observed The lactol **7** or **8** is the only reaction product (>95%) and can be used without further purification In ase of ϵ-caprolactone (**6e**) treatment with dihalomethyllithium led to the corresponding alomethyl)-7-hydroxy-2-heptanone **9** This ring fission is probably due to the instability of the ly formed addition product[12] (Scheme 4 and Table 4)

Table 3. Synthesis of 2-(Dihalomethyl)lactols **7** and **8**

Lactone	Dihalomethane	Product		
		no	Yield,[a]%	mp[b], or R_f
6a	**2a**	**7aa**	60 (55)	70-74
6a	**2b**	**7ab**[c]	71 (66)	74-78[d]
6a	**2c**	**7ac**	77 (70)	75-78
6b	**2a**	**7ba**[c]	65 (58)	58-63[d]
6b	**2b**	**7bb**[c]	68 (61)	66-70[d]
6b	**2c**	**7bc**[c]	80 (75)	74-78[d]
6c	**2a**	**7ca**[c]	68 (65)	0.45[e,f]
6c	**2b**	**7cb**[c]	66 (60)	0 45[e,g]
6c	**2c**	**7cc**[c]	73 (70)	0 47[e,g]
6d	**2a**	**8da**	90 (85)	0 38[h]
6d	**2b**	**8db**[c]	66 (60)	0 37[e,h]
6d	**2c**	**8dc**	73 (68)	0 35[h]

[a] Yield of crude product based on starting lactone **6**, yields of isolated product after purification is given in parenthesis [b] From hexane [c] Mixture of diastereoisomers [d] Of the of mixture diastereoisomers [e] The major diastereoisomer could not be separed by TLC, R_f values refer to the corresponding mixture [f] Hexane/ether 7/3 [g] Hexane/ether 1/1 [h] Hexane/ether 4/1

Table 4 Synthesis of 1-(Dihalomethyl)-7-hidroxy-2-heptanones **9**

Lactone	Dihalomethane	Product		
		no	Yield,[a]%	R_f[b]
6e	**2a**	**9a**	94	0 47
6e	**2b**	**9b**	99	0 44
6e	**2c**	**9c**	97	0 36

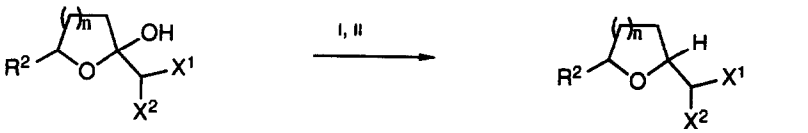
[a] Yield of isolated product based on starting lactone **6d** [b] Ether/hexane 4/1

The possibility of obtaining 2-(dihalomethyl)tetrahydrofurans or pyrans (**10** or **11**) was tested starting from the corresponding lactol **7** or **8** Thus, the reaction of this starting material with triethylsilane in the presence of BF_3 OEt_2[13] yielded **10** or **11** respectively (Scheme 5 and Table 5)

This reaction took place, using the crude lactol **7** or **8** previously prepared, and the isolation of **10** or **11** required only removal of the solvent, without further purification In the case of **7cc**, the mixture

Scheme 4 Reagents. I, Pr^i_2NLi, II, HCl / H_2O

of diastereoisomers of the starting product was 1 1 (NMR) and the *trans/cis* ratio of 2-(dibromomethyl)-5-methyltetrahydrofuran (**10cc**) obtained was 2:1, this stereoselectivity is in agreement with literature data for similar compounds [13] These assignments are supported by ^{13}C NMR data, in general the signals for the *cis* isomer appears at higher field compared to the corresponding *trans* compound,[14]



Scheme 5 Reagents I, $HSiEt_3$, BF_3 OEt_2, II, $NaHCO_3$/ H_2O

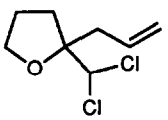
Table 5 Synthesis of 2-(Dihalomethyl)tetrahydrofurans **10** and tetrahydropyrans **11**

	Product		
Lactol	no	Yield,[a]%	R_f[b]
7aa	**10aa**	65	0 45[c]
7ab	**10ab**[d]	81	0 35[e]
7ac	**10ac**	71	0 42
7cc	**10cc**[d]	89	0 42[e]
8dc	**11dc**	73	0 40

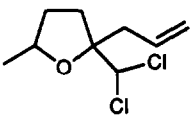
[a] Yield of isolated product based on starting lactol 7 [b] From hexane [c] Hexane/ether 4/1 [d] Mixture of diastereoisomers [e] The major diastereoisomer could not be separated by TLC, R_f values refers to the corresponding mixture

which is attributed to more severe steric compression of substituents in the *cis* compound.[15] In the case of **7ab** stereoselectivity was not observed and the *trans/cis* ratio obtained for product **10ab** was the same as for the mixture of diastereoisomers of the starting material (ca. 1:1).

Finally, the treatment of **7aa** and **7ca** with allyltrimethylsilane in the presence of $BF_3.OEt_2$[15] afforded after removal of the solvents, the corresponding 2-allyl-2-(dichloromethyl)tetrahydrofurans **12aa** and **12ca** respectively, in 50-55% isolated yield (> 96% purity from NMR and GCL) For product **12ca** an ca 3:2 diastereoisomers mixture (NMR, GCL) was obtained



12aa



12ca

EXPERIMENTAL

General Melting points were obtained with a Buchi apparatus Column chromatogrphy was done on Merck grade 60 silica gel (230-400 mesh) and TLC was carried out on Merck 60F-254 precoated silica gel on aluminium sheets IR spectra were determined with a Philips PU-9716 and Perkin-Elmer 1720-XFT spectrometers ^1H and ^{13}C-NMR spectra were recorded on a Bruker AC-300 spectrometer, chemical shifts are given in (ppm) relative to tetramethylsilane as an internal standard, and *J* values are given in Hz Mass spectra were obtained with a Hewlett-Packard 5988A spectrometer Elemental analysis was carried out with a Perkin-Elmer 240 Elemental Analyser Starting dicarboxylic acid diesters, lactones, dichloromethane, bromochloromethane, dibromomethane, triethylsilane, allyltrimethylsilane, dicyclohexylamine and lithium diisopropylamine were of the best commercial grade available (Aldrich) and were used without further purification Solvents were dried before as usually All reactions were carried out under nitrogen and all glassware was dried before use

Preparation of Dihalomethylketoesters **3**. *General Procedure* To a stirred solution of dihalomethane **2** (7 mmol) and the starting diester **1** (5 mmol) in ether (10 ml), was added a solution of lithium dialkylamide (8 mmol) in THF (10 ml) over 5 min at -78 °C Stirring was continued for 5 min at the same temperature and the mixture was hydrolysed with 6N aq HCl (10 ml) Then the solid was filtered, the filtrate was extracted with ether (3 x 5 ml), and the combined layers were dried (Na_2SO_4) The solvents were removed (15 torr) yielding a residue that contains the expected crude ketoester **3** Compound **3** was purified by column chromatography (hexane/ether) on silica gel Yields and R_f values are reported in Table 1 Spectral and analytical data follow

Methyl 5,5-dichloro-4-oxopentanoate (**3aa**). IR (film) 1720 (C=O) cm^{-1}, ^1H-NMR ($CDCl_3$) 2 7 (t, 2H, *J*=6 4, CH_2CO_2), 3 1 (t, 2H, *J*=6 4, CH_2CO), 3 7 (s, 3H, CH_3), 5 9 (s, 1H, CH), ^{13}C-NMR ($CDCl_3$) 27 7 (CH_2CO_2), 30 2 (CH_2CO), 51 8 (CH_3), 69 5 (CH), 172 2 (CO_2), 195 7 (CO), MS, *m/z* 171 (M^+ +4-OCH_3, <1%), 169 (M^+ +2-OCH_3, 10), 167 (M^+-OCH_3,15), 115 (100), 87 (14), 83 (11), 59 (25), 55 (26), Anal Calcd for $C_6H_8Cl_2O_3$ C, 36 21, H, 4 05 Found C, 36 0, H, 4 2

Methyl 7,7-dichloro-6-oxoheptanoate (**3ba**): IR (film) 1720 (C=O) cm^{-1}, ^1H-NMR ($CDCl_3$) 1 6-1 65 (m, 4H, $CH_2CH_2CH_2CO$), 2 3 (t, 2H, *J*=6 4, CH_2CO_2), 2 8 (t, 2H, *J*=6 5, CH_2CO), 3 6 (s, 3H, CH_3), 5 8 (s, 1H, CH), ^{13}C-NMR ($CDCl_3$) 22 9, 23 8 ($CH_2CH_2CH_2CO$), 33 4 (CH_2CO_2), 34 3(CH_2CO), 51 3 (CH_3), 69 6 (CH), 173 3 (CO_2), 196 5 (CO), MS, *m/z* 199 (M^+ +4-OCH_3, <2%), 197 (M^+ +2-OCH_3, 10), 195 (M^+-OCH_3, 15), 143 (45), 115 (17), 111 (100), 83 (35), 73 (33), 59 (34), 55 (47), Anal Calcd for $C_8H_{12}Cl_2O_3$ C, 42 31, H, 5 33 Found C, 41 9, H, 5 2

Ethyl (E)-*5,5-dichloro-4-oxopent-2-enoate* (**3ca**)· IR (film) 1718 (C=O) cm^{-1}, ^1H-NMR ($CDCl_3$) 1 3 (t, 3H, *J*=7 1, CH_3), 4 3 (q, 2H, *J*=7 1, CH_2), 6 0 (s, 1H, $CHCl_2$), 7 0 (d, 1H, *J*=15 7, $CHCO_2$), 7 5 (d, 1H, *J*=15 7, CHCO), ^{13}C-NMR ($CDCl_3$) 14 0 (CH_3), 61 6 (CH_2), 69 0 ($CHCl_2$), 131 8 ($CHCO_2$), 135 7 (CHCO), 164 3 (CO_2), 184 5 (CO), MS, *m/z* 167

(M^+ +2-OC_2H_5, 4%), 165 (M^+-OC_2H_5, 7), 127 (100), 99 (16), 83 (12), 71 (12), 55 (13), 54 (10), 53 (11); Anal Calcd for $C_7H_8Cl_2O_3$· C, 39.84; H, 3.82. Found C, 39.5; H, 3 2.

Ethyl (E)-*5-bromo-5-chloro-4-oxopent-2-enoate* (**3cb**) IR (film) 1719 (C=O) cm^{-1}; ^{1}H-NMR ($CDCl_3$) 1 3 (t, 3H, J=7 1, CH_3), 4.2 (q, 2H, J=7 1, CH_2), 6.0 (s, 1H, CHClBr), 6.9 (d, 1H, J=15.6, $CHCO_2$), 7.5 (d, 1H, J=15 7, CHCO) , ^{13}C-NMR ($CDCl_3$) 13 9 (CH_3), 55 9 (CHBrCl), 61.5 (CH_2), 131 9 ($CHCO_2$), 135 4 (*C*HCO), 164 2 (CO_2), 184.3 (CO), MS, *m/z* 213 (M^+ +4-OC_2H_5, <2%), 211 (M^+ +2-OC_2H_5, 7), 209 (M^+-OC_2H_5, 5), 127 (100), 99 (13), 71 (11), 55 (19), 54 (16), 53 (14), 39 (20), Anal. Calcd. for $C_7H_8BrClO_3$ C, 32.91; H, 3 16. Found C, 32 7; H, 3.3.

Ethyl (E)-*5,5-dibromo-4-oxopent-2-enoate* (**3cc**): IR (film) 1703 (C=O) cm^{-1}; ^{1}H-NMR ($CDCl_3$) 1.3 (t, 3H, J=7 1, CH_3), 4.3 (q, 2H, J=7 1, CH_2), 5 9 (s, 1H, $CHBr_2$), 7 0 (d, 1H, J=15.5, $CHCO_2$), 7 6 (d, 1H, J=15.5, CHCO); ^{13}C-NMR ($CDCl_3$) 14 0 (CH_3), 41 4 ($CHBr_2$), 61.5 (CH_2), 132 0 ($CHCO_2$), 164.3 (CO_2), 184 0 (CO), MS, *m/z* 257 (M^+ +4-OC_2H_5, <1%), 255 (M^+ +2-OC_2H_5, <1), 253 (M^+-OC_2H_5, <1), 127 (100); Anal Calcd for $C_7H_8Br_2O_3$ C, 28 04; H, 2 69 Found C, 27.8, H, 2.7

Methyl o-*(dichloroacetyl)benzoate* (**3da**) IR (film) 1713 (C=O) cm^{-1}, ^{1}H-NMR ($CDCl_3$) 3.8 (s, 3 H, CH_3), 6 4 (s, 1H, $CHCl_2$), 7.5 (dd, 1H, J=1 1 and 7.5 $CHCCO_2$), 7 6 , 7 7 (2dt, 2H, J=1 4 and 7 5, 2x*CH*CHCCO), 8 0 (dd, 1H, J=1 1 and 7 5 CHCCO), ^{13}C-NMR ($CDCl_3$) 52 8 (CH_3), 70.3 ($CHCl_2$), 127.3, 129 0, 129 9, 130 5, 132 9, 138 3 (C_{arom}), 166 1, (CO_2), 192 0 (CO), MS, *m/z* 219 (M^+ +4-OCH_3, <1%,), 217 (M^+ +2-OCH_3, <1), 215 (M^+-OCH_3, <1), 77(21), 76 (14), Anal Calcd for $C_{10}H_8Cl_2O_3$ C, 48 61, H, 3 26 Found C, 48.5, H, 3 1

Methyl o-*(bromochloroacetyl)benzoate* (**3db**): IR (film) 1719 (C=O) cm^{-1}, ^{1}H-NMR ($CDCl_3$) 3 9 (s, 3H, CH_3), 6 4 (s, 1H, CHBrCl), 7 5-8 0 (m, $5H_{arom}$), ^{13}C-NMR ($CDCl_3$) 52 9 (CH_3), 57 8 (CHBrCl), 127 3, 129 8, 130 0, 130 6, 132 9, 138 0 (C_{arom}), 166 0 (CO_2), 192 0 (CO), MS, *m/z* 263 (M^+ +4-OCH_3, <1%), 261 (M^+ +2-OCH_3, <1), 259 (M^+-OCH_3, <1), 164 (10), 163 (100), 133 (14), 104 (11), 77 (23), 76 (20), 50 (13), Anal Calcd for $C_{10}H_8BrClO_3$ C, 41 20, H, 2 77 Found C, 41 0, H, 2 9

Methyl o-*(dibromoacetyl)benzoate* (**3dc**): IR (film) 1708 (C=O) cm^{-1}, ^{1}H-NMR ($CDCl_3$) 3 9 (s, 3H, CH_3), 6 4 (s, 1H, $CHBr_2$), 7 5-8 0 (m, $5H_{arom}$), ^{13}C-NMR ($CDCl_3$) 44 1 ($CHBr_2$), 52 8 (CH_3), 127 1, 129 9, 130 0, 130 4, 132 7, 137 4 (C_{arom}), 165 8 (CO_2), 191 3 (CO), MS, *m/z* 307 (M^+ +4-OCH_3, <1%), 305 (M^+ +2-OCH_3, <1), 303 (M^+-OCH_3, <1), 163 (100), 133 (14), 77 (11), 76 (10), Anal Calcd for $C_{10}H_8Br_2O_3$ C, 35 75, H, 2 40 Found C, 35 4, H, 2 3

Preparation of Tetrahalodiketones **5** *General Procedure* The method was as the same described for **3** but using an excess of dihalomethane **2** (20 mmol) and lithium dialkylamide (22 mmol) Compounds **5** were purified by recrystallization (hexane) Yields and melting points are reported in Table 2 Spectral and analytical data follow

1,1,6,6-Tetrachlorohexan-2,5-dione (**5aa**): IR (KBr) 1732 (C=O) cm^{-1}, ^{1}H-NMR ($CDCl_3$) 3 2 (s, 4H, 2xCH_2), 5 9 (s, 2H, 2xCH), ^{13}C-NMR ($CDCl_3$) 29 3 (2xCH_2), 69 3 (2xCH), 195 5 (2xC=O) , MS, *m/z* 171 (M^+ +4-$CHCl_2$, 10%), 169 (M^+ +2-$CHCl_2$, 62), 167 (M^+-$CHCl_2$, 100), 141 (10), 139 (16), 131 (12), 113 (19), 111 (30), 85 (39), 83 (59), 76 (23), 75 (10), Anal Calcd for $C_6H_6Cl_4O_2$ C, 28 61, H, 2 40 Found C, 28 5, H, 2 4

1,1,8,8-Tetrachlorooctan-2,7-dione (**5ba**): IR (KBr) 1733 (C=O) cm^{-1}, ^{1}H-NMR ($CDCl_3$) 1 7-1 75 (m, 4H, C*H*$_2$C*H*$_2$CH$_2$CO), 2 8-2 9 (m, 4H, 2xCH_2CO), 5 8 (s, 1H, 2xCH), ^{13}C-NMR ($CDCl_3$) 22 8 (*C*H$_2$CH$_2$CH$_2$), 34.3 (2xCH_2CO), 69 7 (2xCH), 196 7 (2xC=O), MS, *m/z* 199 (M^+ +4-$CHCl_2$, 4%), 197 (M^+ +2-$CHCl_2$, 21), 195 (M^+-$CHCl_2$, 32), 169 (17), 167 (26), 123 (12), 113 (19), 111 (12), 103 (18), 97 (19), 95 (11), 91 (13), 89 (10), 87 (11), 85 (63), 83 (100), 79 (30), 78 (12), 77 (23), 76 (32), 75 (16), 67 (42), 56 (14), 55 (47), 53 (12), 48 (13), 43 (15), 42 (16), 41 (37), 39 (24), Anal Calcd for $C_8H_{10}Cl_4O_2$ C, 34 32, H, 3 60 Found C, 34 1, H, 3 7

1,8-Dibromo-1,8-dichlorooctan-2,7-dione (**5bb**) IR (KBr) 1728 (C=O) cm^{-1}, ^{1}H-NMR($CDCl_3$) 1 7-1 75 (m, 4H, C*H*$_2$C*H*$_2$CH$_2$CO), 2 9-2 95 (m, 4H, 2xCH_2CO), 5 9 (s, 1H, 2xCH); ^{13}C-NMR ($CDCl_3$), 22 9 (*C*H$_2$CH$_2$CH$_2$), 34 4 (2xCH_2CO), 56 8 (2xCH), 196 5 (2xC=O); MS, *m/z* 243 (M^+ +4-CHBrCl, 14%), 241 (M^+ +2-CHBrCl, 50), 239 (M^+-CHBrCl, 40), 213 (17), 211 (16), 157 (18), 155(11), 131 (28), 129 (94), 127 (78), 123 (22), 120 (12), 97 (19), 95 (13), 94 (11), 93

(10), 92 (13), 91 (11), 81 (12), 79 (35), 78 (26), 77 (19), 76 (73), 68 (10), 67 (29), 56 (17), 55 (80), 53 (22), 52 (21), 51 (15), 50 (23), 49 (21), 48 (49), 47 (10), 43 (14), 42 (48), 41 (100), 39 (93), Anal Calcd. for $C_8H_{10}Br_2Cl_2O_2$: C, 26 05, H, 2 73 Found C, 25 9; H, 2 7

1,1,8,8-Tetrabromooctan-2,7-dione (**5bc**): IR (KBr) 1718 (C=O) cm^{-1}; ^{1}H-NMR ($CDCl_3$) 1 70-1 75 (m, 4H, $CH_2CH_2CH_2CO$), 2 95-3 0 (m, 4H, $2xCH_2CO$), 5 8 (s, 2H, 2xCH), ^{13}C-NMR ($CDCl_3$) 23 1 ($CH_2CH_2CH_2$), 34.3 ($2xCH_2CO$), 42.7 (2xCH), 196 2 (2xC=O); MS, *m/z* 285 (M^++2-$CHBr_2$, 5%), 207 (18), 205 (16), 175 (13), 173 (31), 171 (12), 125 (23), 123 (100), 122 (21), 121 (88), 120 (17), 107 (14), 97 (38), 93 (51), 94 (17), 95 (50), 92 (15), 81 (39), 79 (39), 69 (13), 68 (10), 67 (11), 56 (16), 55 (69), 53 (19), 43 (36), 42 (64), 41 (70), 39 (45); Anal Calcd for $C_8H_{10}Br_4O_2$ C, 20 99, H, 2 20 Found C, 20 7, H, 2 1

Preparation of 2-(Dihalomethyl) γ*-and* δ*-Lactols* **7**, **8** *and 7-Hidroxy-1-(dihalomethyl)-2-heptanones* **9**. *General Procedure* To a stirred solution of lactone **6** (5 mmol) and dihalomethane **2** (10 mmol) in ether (10 ml) was added a solution of LDA (10 mmol) in THF (10ml) during 5 min at -78 °C After 20 min stirring at the same temperature, the mixture was quenched with 6N aqueous HCl (2ml) Then the solid was filtered, the filtrate was extracted with ether (3 x 5 ml), and the combined layers were dried (Na_2SO_4) The solvents were removed (15 torr) yielding the corresponding products **7**, **8** or **9**. Compounds **7** and **8** can be purified by recrystallization or by column chromatography (hexane/ether) Yields, melting points and R_f values are reported in Tables 3 and 4 Spectral and analytical data follow

2-(Dichloromethyl)-2-hydroxytetrahydrofuran (**7aa**): IR (KBr) 3354 (OH) cm^{-1}, ^{1}H-NMR ($CDCl_3$) 1 9-2 2 (m, 4H, CH_2CH_2C), 3 8 (s, 1H, OH), 4 0-4 2 (m, 2H, CH_2O), 5 7 (s, 1H, CH), ^{13}C-NMR ($CDCl_3$) 24 4, 33 7 (CH_2CH_2C), 69 8 (CH_2O), 75 4 (CH), 106 1 (COH), MS, *m/z* 157 (M^++4-OH, <1%), 155 (M^++2-OH, <1), 153 (M^+-OH, <1), 87 (M^+-$CHCl_2$, 100), 69 (13), 45 (21), 43 (28), 42 (16), 41 (21), Anal Calcd for $C_5H_8Cl_2O_2$ C, 35 11, H, 4 71 Found C, 34 9, H, 4 9

2-(Bromochloromethyl)-2-hydroxytetrahydrofuran (**7ab**): IR (KBr) 3362 (OH) cm^{-1}, ^{1}H-NMR ($CDCl_3$) 2 1-2 2 (m, 4H, CH_2CH_2C), 3 0 (s, 1H, OH), 4 0-4 2 (m, 2H, CH_2O), 5 75, 5 8 (2s, 1H, CH), ^{13}C-NMR ($CDCl_3$) 24 9 (CH_2CH_2CO), 34 3, 34 5 (CH_2COH), 64 2, 64 4 (CH), 70 1 (CH_2O), 105 8, 105 9 (COH), MS, *m/z* 201 (M^++4-OH, <1%), 199 (M^++2-OH, <1), 197 (M^+-OH, <1), 87 (M^+-CHBrCl, 100), 45 (13), 43 (18), 42 (10), 41 (14), Anal Calcd for $C_5H_8BrClO_2$ C, 27 87, H, 3 74 Found C, 27 5, H, 3 9

2-(Dibromomethyl)-2-hydroxytetrahydrofuran (**7ac**) IR (KBr) 3365 (OH) cm^{-1}, ^{1}H-NMR ($CDCl_3$) 2 0-2 3 (m, 4H, CH_2CH_2C), 3 0 (s, 1H, OH), 4 0-4 2 (m, 2H, CH_2O), 5 7 (s, 1H, CH), ^{13}C-NMR ($CDCl_3$) 25 0, 34 7 (CH_2CH_2C), 51 0 (CH), 70 1 (CH_2O), 105 5 (COH), MS, *m/z* 175 ($CHBr_2$+4, 2%), 173 ($CHBr_2$+2, 4), 171 ($CHBr_2$, 2), 87 (M^+-$CHBr_2$, 100), 45 (14), 43 (22), 42 (11), 41 (16), Anal Calcd for $C_5H_8Br_2O_2$ C, 23 10, H, 3 10 Found C, 22 8, H, 3 3

3-Bromo-2-(dichloromethyl)-2-hydroxytetrahydrofuran (**7ba**) IR (KBr) 3426 (OH) cm^{-1}, ^{1}H-NMR ($CDCl_3$) 2 2-2 8 (m, 2H, CH_2CHBr), 2 9-3 1 (m, 1H, CHBr), 3 5-3 7 (1s, 1H, OH), 3 9-4 7 (m, 2H, CH_2O), 5 9, 6 2 (2s, 1H, $CHCl_2$), ^{13}C-NMR ($CDCl_3$) 34 8, 35 1 (CH_2CHBr), 46 7, 52 5 (CHBr), 67 2, 68 4 (CH_2O), 73 2, 75 8 ($CHCl_2$), 102 7, 106 0 (COH), MS, *m/z* 167 (M^++2-$CHCl_2$, 58%), 165 (M^+-$CHCl_2$, 57), 122 (57), 120 (52), 87 (5), 85 (44), 83 (19), 76 (13), 75 (12), 57 (15), 55 (16), 41 (100), 39 (25), Anal Calcd for $C_5H_7BrCl_2O_2$ C, 24 03, H, 2 82 Found C, 23 8, H, 3 0

3-Bromo-2-(bromochloromethyl)-2-hydroxytetrahydrofuran (**7bb**): IR (KBr) 3400 (OH) cm^{-1}, ^{1}H-NMR ($CDCl_3$) 2 2-2 8 (m, 2H, CH_2CHBr), 3 0-3 1 (m, 1H, CHBr), 3 4-3 7 (m, 1H, OH), 4 0-4 7 (m, 2H, CH_2O), 5 85, 5 9, 6 2, 6 3 (4s, 1H, CHBrCl), ^{13}C-NMR ($CDCl_3$) 34 7, 35 0, 35 4 (CH_2CHBr), 45 9, 47 5, 51 9, 53 3 (CHBr) 61 0, 61 4, 63 5, 64 6 (CHBrCl), 67 0, 67 1, 68 1, 68 6 (CH_2O), 102 2, 102 4, 105 7, 105 8 (COH), MS, *m/z* 167 (M^++2-CHBrCl, 97%), 165 (M^+-CHBrCl, 100), 139 (13), 137 (14), 131 (CHBrCl+4, 5), 129 (CHBrCl+2, 16), 127 (CHBrCl, 12), 122 (69), 121 (13), 120 (69), 109 (13), 107 (15), 85 (35), 76 (13), 57 (16), 55 (19), 41 (86), 39 (28), 31 (13), Anal Calcd for $C_5H_7Br_2ClO_2$ C, 20 40, H, 2 40 Found C, 20 1, H, 2 6

3-Bromo-2-(dibromomethyl)-2-hydroxytetrahydrofuran (**7bc**): IR (KBr) 3430 (OH) cm^{-1}, ^{1}H-NMR ($CDCl_3$) 2 3-2 8 (m, 2H, CH_2CHBr), 3 0-3 1 (m, 1H, CHBr), 3 9-4 8 (m, 3H, CH_2O and OH), 5 8, 6 1 (2s, 1H, $CHBr_2$), ^{13}C-NMR ($CDCl_3$) 34 7, 35 2 (CH_2CHBr), 46 6, 47 2 (CHBr), 50 3, 52 7 ($CHBr_2$), 66 8, 68 2 (CH_2O), 101 7, 105 2 (COH), MS, *m/z* 175 ($CHBr_2$+4, 7%), 173 ($CHBr_2$+2, 14), 171 ($CHBr_2$, 6), 167 (M^++2-$CHBr_2$, 92), 165 (M^+-$CHBr_2$, 100), 139 (14), 137 (16), 122 (52), 121

(14), 120 (55), 109 (14), 107 (15), 94 (12), 93 (12), 92 (12), 85 (25), 57 (15), 55 (18), 41 (67), 39 (27), 31 (17), Anal Calcd for $C_5H_7Br_3O_2$ C, 17 72; H, 2.08 Found C, 17 4; H, 2 2.

2-(Dichloromethyl)-2-hydroxy-5-methyltetrahydrofuran (**7ca**): IR (film) 3393 (OH) cm^{-1}, ^{1}H-NMR ($CDCl_3$) 1 2, 1 3 (2d, 3H, J=6.2 and 6 1 CH_3), 1.5-2.4 (m, 4H, CH_2CH_2), 3 2 (s, 1H, OH), 4 2-4.5 (2m, 1H, CHO), 5 70, 5 75 (2s, 1H, $CHCl_2$), ^{13}C-NMR ($CDCl_3$) 20.2, 21.5 (CH_3), 32 0, 34 0, 34 4 (CH_2CH_2C), 75 4, 75.8 ($CHCl_2$), 76 9, 79.5 (CH_3CHO), 105 9, 106 1 (COH), MS, *m/z* 101 (M^+-$CHCl_2$, 47%), 87 ($CHCl_2$+4, 12), 85 ($CHCl_2$+2, 52), 85 ($CHCl_2$+2, 51), 83 ($CHCl_2$, 100), 76 (19), 59 (15), 57 (17), 56 (29), 55 (70), 53 (11), 51 (14), 50 (26), 49 (18), 48 (48), 47 (18), 45 (73), 44 (12), 43 (94), 42 (39), 41(76), 40 (22), 39 (68), 38 (12), 37 (12); Anal. Calcd. for $C_6H_{10}Cl_2O_2$ C, 38 94; H, 5 45 Found C, 38.7, H, 5 7

2-(Bromochloromethyl-2-hydroxy-5-methyltetrahydrofuran (**7cb**): IR (film) 3397 (OH) cm^{-1}; ^{1}H-NMR ($CDCl_3$) 1 2, 1 3, 1 4 (3d, 3H, J=6 1, CH_3), 1 6-2.4 (m, 4H, CH_2CH_2), 3 2 (s, 1H, OH), 4 3-4 6 (m, 2H,CHO), 5 73, 5,74, 5,75 5,76 (4s, 1H, CHBrCl); ^{13}C-NMR ($CDCl_3$) 20.2, 21.5 (CH_3), 32 1, 32.2, 32.3, 34 1, 34.3, 34 6, 34.8 (CH_2CH_2), 64 1, 64 2, 64 6 (CHBrCl), 76 9, 79.5 (CHO), 105.6, 105.7, 105.8 (COH), MS, *m/z* 131 (CHBrCl+4, 7%), 129 (CHBrCl+2, 26), 127 (CHBrCl, 21), 101 (M^+-CHBrCl, 63), 83 (18), 79 (10), 76 (12), 59 (13), 57 (12), 56 (22), 55 (59), 53 (11), 51 (12), 50 (14), 48 (21), 45 (48), 44 (11), 43 (100), 42 (31), 41 (63), 40 (30), 39 (59), Anal. Calcd for $C_6H_{10}BrClO_2$ C, 31 40, H, 4 39 Found C, 31 2; H, 4 5

2-(Dibromomethyl)-2-hydroxy-5-methyltetrahydrofuran (**7cc**): IR (film) 3397 (OH) cm^{-1}; ^{1}H-NMR ($CDCl_3$) 1 2, 1 3 (2d, 3H, J=6 1, CH_3), 1 6-2.4 (m, 4H, CH_2CH_2), 3 1 (s, 1H, OH), 4 3-4 6 (m, 1H, CHO), 5 70, 5 75 (2s, 1H, $CHBr_2$), ^{13}C-NMR ($CDCl_3$) 20.3, 21 6 (CH_3), 32.3, 32 5, 34 5, 35 1 (CH_2CH_2), 51 1, 51 5 ($CHBr_2$), 77 0, 79 5 (CHO), 105 2, 105 4 (COH), MS, *m/z* 175 ($CHBr_2$+4, 7%), 173 ($CHBr_2$+2, 15), 171 ($CHBr_2$, 8), 122 (10), 120 (10), 101 (M^+-$CHBr_2$, 100), 94 (13), 93 (10), 92 (16), 83 (28), 81 (16), 79 (11), 59 (14), 57 (13), 56 (18), 55 (62), 53 (11), 45 (60), 44 (10), 43 (80), 42 (29), 41 (64), 40 (18), 39 (52), Anal Calcd for $C_6H_{10}Br_2O_2$ C, 26 31, H, 3 68 Found C, 26 1, H, 3 8

2-(Dichloromethyl)-2-hydroxytetrahydropyran (**8da**): IR (film) 3420 (OH) cm^{-1}, ^{1}H-NMR ($CDCl_3$) 1 5-2 0 (m, 6H, $CH_2CH_2CH_2C$), 2.8 (s, 1H, OH), 3.8-4 0 (m, 2H, CH_2O), 5 6 (s, 1H, CH), ^{13}C-NMR ($CDCl_3$) 18 4, 24 3, 29 4 ($CH_2CH_2CH_2C$), 62 2 (CH_2O), 77 6 (CH), 95.8 (COH), MS, *m/z* 126 (M^+-C_4H_{10}, 10%), 101 (M^+-$CHCl_2$, 100), 85 (17), 83 (73), 76 (11), 59 (19), 57 (24), 56 (81), 55 (85), 43 (25), 42(16), 41 (44), 39 (23), Anal Calcd for $C_6H_{10}Cl_2O_2$ C, 38 94, H, 5 45 Found C, 38 7, H, 5 6

2-(Bromochloromethyl)-2-hydroxytetrahydropyran (**8db**): IR (film) 3426 (OH) cm^{-1}, ^{1}H-NMR ($CDCl_3$) 1 5-2 0 (m, 6H, $CH_2CH_2CH_2C$), 2.8 (s, 1H, OH), 3 8-4 0 (m, 2H, CH_2O), 5 60, 5 65 (2s, 1H, CHBrCl), ^{13}C-NMR ($CDCl_3$) 18 5, 24 1, 24 2, 29 2, 29.3 ($CH_2CH_2CH_2C$), 62 2 (CH_2O), 66 7, 67 1 (CHBrCl), 95 2, 95 3 (COH), MS, *m/z* 131 (CHBrCl+4, 3%), 129 (CHBrCl+2, 14), 127 (CHBrCl, 10), 101 (M^+-CHBrCl, 100), 91 (14), 83 (56), 76 (11), 59 (15), 57 (30), 56 (45), 55 (80), 43 (28), 42 (16), 41 (28), 40 (16), 39 (17), Anal Calcd for $C_6H_{10}BrClO_2$ C, 31 40, H, 4 39 Found C, 31 1, H, 4 5

2-(Dibromomethyl)-2-hydroxytetrahydropyran (**8dc**): IR (film) 3441 (OH) cm^{-1}; ^{1}H-NMR ($CDCl_3$) 1 5-2 0 (m, 6H, $CH_2CH_2CH_2C$), 2 8 (s, 1H, OH), 3 8-4 0 (m, 2H, CH_2O), 5 6 (1s, 1H, CH), ^{13}C-NMR ($CDCl_3$) 19 1, 24 4, 30 0 ($CH_2CH_2CH_2C$), 54 6 (CH), 62 7 (CH_2O), 94 9 (COH), MS, *m/z* 175 ($CHBr_2$+4, 5%), 173 ($CHBr_2$+2, 10), 171 ($CHBr_2$, 5), 122 (10), 120 (10), 101 (M^+-CHBr, 100), 83 (51), 59 (11), 57 (22), 56 (13), 55 (66), 43 (21), 42 (11), 41 (17), 39 (11), Anal Calcd for $C_6H_{10}Br_2O_2$ C, 26 31, H, 3 68 Found C, 26 1, H, 3 8

1,1-Dichloro-7-hydroxyheptan-2-one (**9a**): IR (film) 3387 (OH), 1729 (C=O) cm^{-1}, ^{1}H-NMR ($CDCl_3$) 1 2-1 6 (m, 6H, $CH_2CH_2CH_2CH_2O$), 2 6 (t, 2H, J=7 2, CH_2CO), 3 4 (t, 2H, J=6 4, CH_2OH), 4 7 (s, 1H, OH), 5 7 (s, 1H, CH), ^{13}C-NMR ($CDCl_3$) 23 2, 24 8, 31 8, 34 9 ($CH_2CH_2CH_2CH_2CO$), 61 8 (CH_2OH), 69 6 (CH), 197 1 (CO), MS, *m/z* 115 (M^+-$CHCl_2$, 14%), 97 (26), 85 (14), 83 (17), 79 (15), 76 (12), 73 (17), 69 (100), 55 (41), 43 (20), 42 (13), 41 (76), 39 (28), Anal Calcd for $C_7H_{12}Cl_2O_2$ C, 42 23, H, 6 07 Found C, 42 0, H, 6 2

1-Bromo-1-chloro-7-hydroxyheptan-2-one (**9b**): IR (film) 3382 (OH), 1734 (C=O) cm^{-1}, ^{1}H-NMR ($CDCl_3$) 1 3-1 9 (m, 6H, $CH_2CH_2CH_2CH_2O$), 2.9 (t, 2H, J=7 2, CH_2CO), 3 7 (t, 2H, J=6 5, CH_2OH) 5 2 (s, 1H, OH), 5 8 (s, 1H, CH), ^{13}C-NMR ($CDCl_3$) 23 5, 24 8, 31 9, 34 8 ($CH_2CH_2CH_2CH_2CO$), 56 9 (CH), 62 0 (CH_2OH), 197 0 (CO), MS, *m/z* 131 (CHBrCl+4, 4%), 129 (CHBrCl+2, 16), 127 (CHBrCl, 12), 115 (16), 97 (28), 79 (16), 76 (21), 73 (15), 69 (80), 57 (12), 55 (46), 53 (14), 50 (11), 48 (17), 43 (28), 42 (24), 41 (100), 40 (10), 39 (68), Anal Calcd for $C_7H_{12}BrClO_2$ C, 34 52, H, 4 97 Found C, 34 2, H, 5 2

1,1-Dibromo-7-hidroxyheptan-2-one (**9c**): IR (film) 3376 (OH), 1719 (C=O) cm^{-1}, ^{1}H-NMR ($CDCCl_3$) 1 3-1 7 (m, 6H, $CH_2CH_2CH_2CH_2O$), 2.6 (s, 1H, OH), 2 9 (t, 2H, J=7 2, CH_2CO), 3.6 (t, 2H J= 6.5, CH_2OH), 5.8 (s, 1H, CH), ^{13}C-NMR ($CDCl_3$) 23.8, 24.8, 32.0, 34.7 ($CH_2CH_2CH_2CH_2CO$) 42 8 (CH), 62.0 (CH_2OH), 196.8 (CO), MS, *m/z* 175 ($CHBr_2$+4, 7%), 173 ($CHBr_2$+2, 15), 171 ($CHBr_2$, 7), 122 (17), 120 (17), 115 (22), 97 (30), 94 (13), 92 (13), 79 (15), 73 (13), 69 (65), 57 (12), 55 (41), 53 (14), 43 (27), 42 (25), 41 (100), 40 (11), 39 (75), Anal Calcd for $C_7H_{12}Br_2O_2$ C, 29 20, H, 4 20 Found C, 29 0, H, 4 4

Preparation of 2-Dihalomethyltetrahidrofurans **10**, *2-Dihalomethyltetrahidropyrans* **11** *and 2-Allyl-2-(dichloromethyl)tetrahydrofurans* **12.** To a stirred solution of ɣ- or δ- lactol **7** or **8** (4 mmol) in dichloromethane (20 ml) was added triethylsilane or allyltrimethylsilane (16 mmol) and BF_3OEt_2 (24 mmol) at -78 °C Stirring was continued for 1h at the same temperature and them over night allowing it to warm to room temperature The mixture was hidrolysed with saturated aqueous $NaHCO_3$ (5 ml), extracted with dichloromethane (3 x 5 ml) and the combined layers were dried (Na_2SO_4) The solvents were removed (15 torr) yielding a residue that contained the expected crude products **10, 11** or **12** with more than 96 % purity (NMR, CGL) Yields and R_f values of products **10** and **11** are reported in Table 5 Spectral and analytical data follow

2-(Dichloromethyl)tetrahydrofuran (**10aa**) IR (film) 1069 (CO) cm^{-1}, ^{1}H-NMR ($CDCCl_3$) 1 8-2 1 (m, 4H, CH_2CH_2CH), 3.8-4 0 (m, 2H, CH_2O), 4 2-4 3 (m, 1H, CHO), 5 6 (d, 1H, J=5 7, $CHCl_2$), ^{13}C-NMR ($CDCl_3$)25 8, 27 6 (CH_2CH_2CH), 69 7 (CH_2O), 74 2 ($CHCl_2$), 82 6 (CHO), MS, *m/z* 87 ($CHCl_2$+4, 3%), 85 ($CHCl_2$+2, 14), 82 ($CHCl_2$, 23), 71 (C_4H_7O, 100), 53 (15) ,51 (11), 49 (15), 48 (12), 43 (45), 42 (19), 41 (41), 40 (11), 39 (37), Anal Calcd for $C_5H_8Cl_2O$ C, 38 74 , H, 5 20 Found C, 38.5; H, 5 4

2-(Bromochloromethyl)tetrahydrofuran (**10ab**) IR (film) 1061 (CO) cm^{-1}, ^{1}H-NMR ($CDCCl_3$) 1 8-2 2 (m, 4H, CH_2CH_2CH), 3 8-4 0 (m, 2H, CH_2O), 4 2-4 3 (m, 1H, CHO), 5 7 (d, 1H, J=4 6, CHBrCl), ^{13}C-NMR ($CDCl_3$) 25 7, 25 8, 27 8 28 7 (CH_2CH_2CH), 62 2, 62 9 (CHBrCl), 69 5, 69 7 (CH_2O), 82 6, 82 7 (CHO), MS, *m/z* 200 (M^++2, 4%), 198 (M^+, 24), 157 (11), 155 (15), 142 (16), 140 (15), 131 (CHBrCl+4, 28), 129 (CHBrCl+2, 100), 127 (CHBrCl, 77), 123 (20), 122 (24), 121 (32), 120 (28), 119 (35), 108 (11), 107 (25), 106 (12), 105 (22), 71 (C_4H_7O, 85), 43 (11), Anal Calcd for C_5H_8BrClO C, 30 11, H, 4 04 Found C, 30 0, H, 4 2

2-(Dibromomethyl)tetrahydrofuran (**10ac**) IR (film) 1060 (CO) cm^{-1}, ^{1}H-NMR ($CDCCl_3$) 1 9-2 3 (m, 4H, CH_2CH_2CH), 3 9-4 0 (m, 2H, CH_2O), 4 2-4 3 (m, 1H, CHO), 5 7 (d, 1H, J=4 7, $CHBr_2$), ^{13}C-NMR ($CDCl_3$) 26 0, 29 3 (CH_2CH_2CH), 49 3 ($CHBr_2$), 69 9 (CH_2O), 82 9 (CHO), MS, *m/z* 244 (M^++2, 2%), 71 (C_4H_7O, 100), 43 (18), 41 (11), Anal Calcd for $C_5H_8Br_2O$ C, 24 62, H, 3 31 Found C, 24.3, H, 3 5

2-(Dibromomethyl)-5-methyltetrahydrofuran (**10cc**) IR (film) 1084 (CO) cm^{-1}, ^{1}H-NMR ($CDCCl_3$) 1 2, 1 3 (2d, 3H, J=6 0, CH_3), 2 0-2 4 (m, 4H, 2xCH_2), 4 1-4 5 (m, 2H, 2xCHO), 5 6, 5 7 (2d, 1H, J=5 7, $CHBr_2$), ^{13}C-NMR ($CDCl_3$) 20 6, 20 8 (CH_3), 29 3, 29 7, 32 6, 33 8 (2xCH_2) 49 1, 50 1 ($CHBr_2$), 77 2 ,77 5 ($CHOCH_3$), 82 5, 83 0 ($CHCHBr_2$), MS, *m/z* 175 ($CHBr_2$+4, 3%), 173 ($CHBr_2$+2, 6), 171 ($CHBr_2$, 3), 95 (14), 94 (11), 93 (16), 92 (10), 85 (C_5H_9O, 100), 83 (13), 82 (10), 81 (47), 79 (18), 67 (15), 57 (18), 55 (20), 53 (60), 52 (10), 51 (25), 50 (18), 43 (82), 42 (34), 41 (75), 40 (15), 39 (89), 38 (19), Anal Calcd for $C_6H_{10}Br_2O$ C, 27 94 , H, 3 91 Found C, 27 6 , H, 4 1

2-(Dibromomethyl)tetrahydropyran (**11dc**) IR (film) 1074 (CO) cm^{-1}, ^{1}H-NMR ($CDCCl_3$) 1 5-2 0 (m, 6H, $CH_2CH_2CH_2CH$), 3 5-3 6 (m, 2H, CH_2O), 4 1-4 15 (m, 1H, CHO), 5 6 (d, 1H, J=4 2, $CHBr_2$), ^{13}C-NMR ($CDCl_3$) 22 2, 25 0, 27 5 ($CH_2CH_2CH_2CH$), 47 6 ($CHBr_2$), 68 6 (CH_2O), 80 8 (CHO), MS, *m/z* 85 (M^+-$CHBr_2$, 100%), 41 (12), Anal Calcd for $C_6H_{10}Br_2O$ C, 27 94 , H, 3 91 Found C, 27 7, H,4 1

2-Ally-2-(dichloromethyl)tetrahydrofuran (**12aa**) R_f=0 47 (hexane), IR (film) 3078, 1641 (CH_2=CH), 1056 (CO) cm^{-1}, ^{1}H-NMR ($CDCCl_3$) 1 8-2 3 (m, 4H, CH_2CH_2C), 2 4-2 6 (m, 2H, CH_2CH=C), 3 95, 4 0 (2d, 2H, J=5 8, CH_2O), 5 15, 5 2 (2d, 2H, J=6 0 and 10 0, CH_2=CH), 5 7 (s, 1H, $CHCl_2$), 5 8-5 9 (m, 1H, CH=CH_2), ^{13}C-NMR ($CDCl_3$) 26 4, 31 5 (CH_2CH_2C), 41 0 (CH_2CH=C), 70 3 (CH_2O), 78 0 ($CHCl_2$), 87 8 (CO), 119.2 (CH_2=CH), 132 4 (CH=CH_2), MS, *m/z* 157 (M^++4-CH_2CH=CH_2, 10%), 155 (M^++2-CH_2CH=CH_2, 56), 153 (M^+-CH_2CH=CH_2, 81), 113 (16), 111 (64), 87 ($CHCl_2$+4, 17),

85 ($CHCl_2$+2, 42), 83 ($CHCl_2$, 64), 76 (15), 69 (26), 65 (11), 63 (11), 53 (24), 51 (18), 42 (26), 41 (100), 40 (27), 39 (90), 38 (11), Anal Calcd for $C_8H_{12}Cl_2$ C, 49 25, H, 6 20 Found C, 49 0; H, 6 5

2-Allyl-2-(dichloromethyl)-5-methyltetrahydrofuran (**12ca**) R_f=0 4 (hexane), IR (film) 3079, 1642 (CH_2=CH), 1078 (CO)cm^{-1}; ^{1}H-NMR ($CDCCl_3$) 1 2 (2d, 3H, *J*=6 0, CH_3), 1 8-2.3 (m, 4H, CH_2CH_2C), 2 4-2.5 (m, 2H, CH_2CH=C), 4 1-4 2 (m, 1H, CHO), 5 0-5 1 (m, 2H, CH_2=CH),5 6, 5 7 (2s, 1H, $CHCl_2$), 5 7-5 8 (m, 1H, CH=CH_2), ^{13}C-NMR ($CDCl_3$) 20 55, 20 6 (CH_3), 31 9, 32 3, 33.85, 33 9 (CH_2CH_2C), 41 0 (CH_2CH=C), 77 4, 77 6 (CHO), 77 9, 78 5 ($CHCl_2$), 87 9 (CO), 119 0, 119 2 (CH_2=CH), 132.5, 132 6 (CH=CH_2), , MS, *m/z* 171 (M^++4-CH_2CH=CH_2, 4%), 169 (M^++2-CH_2CH=CH_2, 28), 167 (M^+-CH_2CH=CH_2, 43), 125 (14), 91 (10), 87 ($CHCl_2$+4, 5), 85 ($CHCl_2$+2, 22), 83 ($CHCl_2$, 39), 77 (17), 69 (13), 67 (23), 65 (14), 56 (12), 55 (30), 53 (22), 51 (17), 43 (39), 42 (19), 41 (100), 40 (13), 39 (94) Anal Calcd. for $C_9H_{14}Cl_2O$ C, 51 69, H, 6 75 Found C, 51 4, H, 6 9 [16]

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16 We thank Dr P Bernad (Servicio de Espectroscopía de Masas, Universidad de Oviedo) for spectrometric mass determinations