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Highly Diastereoselective Synthesis of Substituted Epichlorohydrins and Regioselective Preparation of Allyl Alcohols using Chloro or Iodomethyllithium.

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Abstract: Substituted epichlorohydrins **3** or **6** are obtained from α-bromo or α-chlorocarbonyl compounds (**1** or **4**) and chloro or iodomethyllithium, respectively. Starting from α-bromocarbonyl compounds **1** or acyclic α-chloro ketones the reaction takes place with total diastereoselectivity. Treatment of epichlorohydrins **3** or **6** with lithium iodide affords the same substituted allyl alcohols **7** in a regioselective manner. A mechanism to explain this transformation is proposed. Regioisomeric allyl alcohols **11** are prepared by reaction of epichlorohydrins **6** with lithium powder.

INTRODUCTION

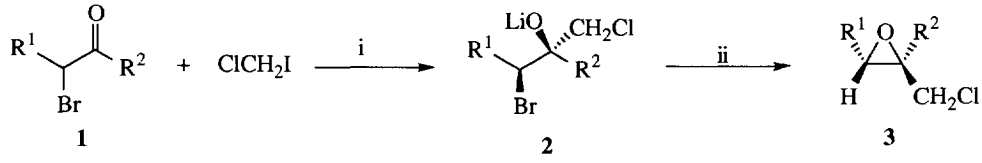
The oxirane ring opening of chloromethyloxirane (epichlorohydrin) with several nucleophiles (such as DIBAL[1], carboxylic acids[2], potassium cyanide[3], benzenethiol[4], organolithium compounds[5] and Grignard reagents[6]) is an important synthetic transformation which gives an easy access to a large number of functionalized intermediates that are required during the synthesis of natural products. Several rearrangement processes of epichlorohydrin lead also to useful synthetic intermediates such as 1-alken-3-ols[7] and 1-alkyn-3-ols[8]. On the other hand, allyl alcohols are useful building blocks for organic synthesis. So, the Sharpless asymmetric epoxidation of these compounds has proven to be an extremely useful method of synthesizing enantiomerically enriched compounds[9]. However, to the best of our knowledge, there is not a general and direct[10] methodology for the synthesis of substituted epichlorohydrins and the synthesis of substituted allyl alcohols presents the usual problems associated with regioselectivity in the allylic moiety[11].

Recently, we reported the synthesis with total diastereoselectivity of 2,3-disubstituted-2-chloromethyloxiranes (disubstituted epichlorohydrins), and their further transformation into substituted allyl alcohols, starting from α-bromocarbonyl compounds and chloromethyllithium[7a]. In the present paper we describe a general method for the preparation of substituted epichlorohydrins by reaction of α-bromo or α-chlorocarbonyl compounds with chloro or iodomethyllithium respectively.

RESULTS AND DISCUSSION

a) Synthesis of substituted epichlorohydrins

The reaction of different α-bromocarbonyl compounds **1** with chloromethyllithium (generated *in situ*[12] by treatment of chloroiodomethane with methyllithium at -78°C) gave the corresponding 2,3-disubstituted-2-chloromethyloxirane **3** when the reaction mixture was allowed to warm to room temperature (Scheme 1 and Table 1).



Scheme 1. *Reagents and conditions*: i, MeLi/LiBr, -78°C; ii,-78 to 20°C.

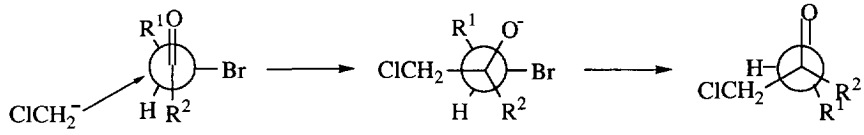
The reaction took place with total diastereoselectivity: thus NMR analysis (300 or 75 MHz) of the reaction crude showed the presence of only one diastereoisomer. The stereochemistry of products **3a-d** was determined by NOE experiments. In the case of compound **3e** was assigned by the value of coupling constant between the oxirane protons and according to the coupling constants for *trans*-oxiranes[13]. In all products **3** the stereochemistry was found S*, R* or *unlike* (*u*)[14].

Table 1. Diastereoselective Preparation of Substituted Epichlorohydrins **3** from α-Bromocarbonyl Compounds **1**.

	α-Bromocarbonyl Compound **1**				
Entry	R^1	R^2	Product	% Yield[a]	R_f (hexane)
1	Me	Me	**3a**	62	0.47
2	Me	Ph	**3b**	89	0.40
3	n-Bu	H	**3c**	75	0.53
4	n-Bu	n-Pr	**3d**	91	0.33
5	n-C_6H_{13}	H	**3e**	77	0.41

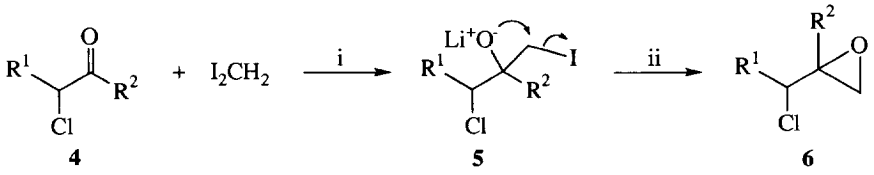
[a] Isolated yield based on the starting carbonyl compound **1**.

A Felkin-Anh model[15] can explain the observed stereochemistry since the energetically more favoured transition state has the larger and more polar substituent (bromine) anti to the attack path of chloromethyllithium[16] according to a Bürgi-Dunitz trajectory for the approach[17] (Scheme 2).



Scheme 2.

In order to expand the generality of the synthesis of substituted epichlorohydrins, we have also prepared regioisomer epichlorohydrins **6** by reaction of α-chlorocarbonyl compounds **4** with iodomethyllithium. Thus, the reaction of different α-chlorocarbonyl compounds **4** with iodomethyllithium (generated *in situ* by treatment of diiodomethane with methyllithium at -78°C) gave the corresponding epichlorohydrins **6** when the reaction mixture was allowed to reach room temperature (Scheme 3 and Table 2). The best results were obtained using THF as solvent and when the iodomethyllithium/carbonyl compound ratio was 2/1. Moreover, when all iodomethyllithium was generated at once, about 40% of unreacted carbonyl compound was isolated. The α-chlorocarbonyl compound reacted completely by addition of CH_2I_2 (and subsequently MeLi) in several portions (see Experimental Part).



Scheme 3. *Reagents and conditions*: i, MeLi; ii, -78 to 20°C.

In contrast to the case of epichlorohydrins **3**, the stereochemistry of this process depends on the starting carbonyl compound. So, the reaction took place diastereoselectively in the case of acyclic ketones (Table 2, entries 1 and 6) and in the other cases a mixture of diasteroisomers was isolated (Table 2).

When the reaction was carried out with cyclic ketones (Table 2, entries 7 and 8) the major diastereoisomer was the *u* epichlorohydrin in which the chloro atom is syn to the oxygen group. The stereochemistry observed was in agreement with the literature data for the nucleophilic addition of bulky nucleophiles to α-substituted cycloalkanones[18]. These assignments are supported by ^{13}C NMR data; in general the signals of the *cis* isomer appears at higher field compared to the corresponding *trans* compound[19]. The stereochemistry of the other products (**6a-f**) was not assigned.

Table 2. Preparation of Substituted Epichlorohydrins **6** from α-Chlorocarbonyl Compounds **4**.

	α-Chlorocarbonyl Compound **4**					
Entry	R^1	R^2	Product	% Yield[a]	Diastereomeric excess[b]	R_f[c]
1	Me	Me	**6a**	60	>98	0.54
2	Et	H	**6b**	75	54	0.42[d]
3	n-Pr	H	**6c**	90	24	0.62[e]
4	i-Pr	H	**6d**	70	14	0.43
5	n-Bu	H	**6e**	85	56	0.37
6	n-Bu	n-Pr	**6f**	64	>98	0.45
7	$-(CH_2)_3-$		**6g**	90	70	0.40
8	$-(CH_2)_4-$		**6h**	89	72	0.38

[a] Isolated yield based on the starting carbonyl compound **4**. [b]The diastereomeric excess was determined from ^1H and ^{13}C NMR data. [c]Hexane. [d]Hexane/ether : 4/1. [e]Hexane/ether : 2/1.

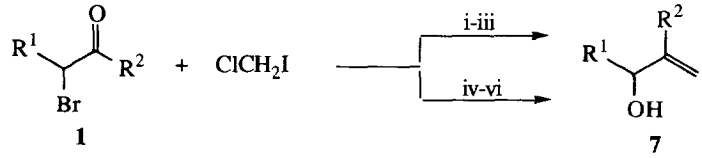
On the other hand, it seems that the diastereoselectivity level is better with α-bromocarbonyl compounds than with α-chlorocarbonyl ones. A possible explanation can be that the polar group is also the largest substituent in α-bromocarbonyl compounds while in α-chlorocarbonyl compounds the chloro atom is not the largest substituent[20]. Thus, in a Felkin-Anh model for α-chlorocarbonyl compounds (Scheme 4) there are two possible topicities: with the most polar substituent (figure **A**) or with the largest substituent (figure **B**) anti to the attack path of iodomethyllithium. The high levels of 1,2-asymmetric induction observed with acyclic ketones (Table 2, entries 1 and 6) and not extended to aldehydes, was in agreement with previous studies[20,21].

Scheme 4.

In summary, the present methodology is general since epichlorohydrins can be obtained in a regioselective manner from α-bromo or α-chloro aliphatic and aromatic ketones and aldehydes. In addition, the process takes place with total diastereoselectivity starting from α-bromocarbonyl compounds and acyclic α-chloroketones, and the isolation of epichlorohydrins requires only removal of the solvents, without further purification. We think that the epoxidation of α-chlorocarbonyl compounds using iodomethyllithium represents a convenient method since the same reaction using sulphur ylides is not possible[22].

b) Synthesis of substituted allyl alcohols

The reaction of different α-bromocarbonyl compounds **1** with chloromethyllithium (generated *in situ* at -78°C) in the presence of lithium iodide led, after warming, evaporation under reduced pressure and final hydrolysis, to 1,2-disubstituted allyl alcohols **7** (Scheme 5 and Table 3), two reactive functions being generated in this process. The same results were obtained starting from the isolated epichlorohydrins **3**. The mechanism proposed (Scheme 6) involves the initial formation of the epichlorohydrin **3** and the further nucleophilic substitution of chlorine by iodine yielding the iodoepoxide **8**. The halophilic attack of a second iodide to **8** induced a β-elimination reaction by opening of the oxirane ring yielding, after hydrolysis, the allyl alcohol **7**. A similar elimination *via* a vicinal diiodide in the presence of iodide, has been already reported[23].



Scheme 5. *Reagents and conditions*: i, MeLi/LiI, -78°C; ii, 20 to 60°C, then evaporation: iii, NH_4Cl-H_2O; iv, MeLi/LiBr, -78°C; v, Li, -78 to 20°C; vi, HCl-H_2O.

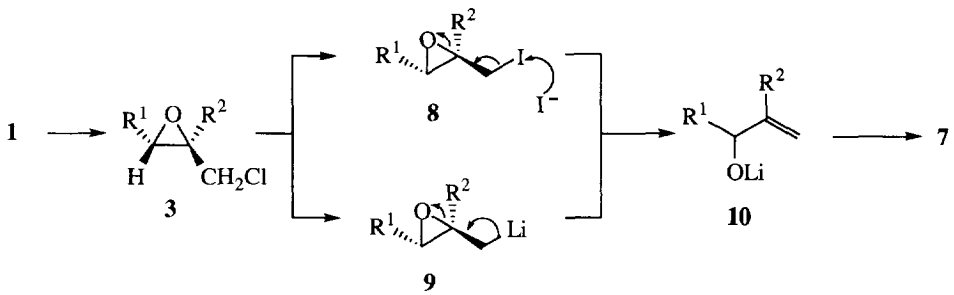
The yields for the transformation of epichlorohydrins **3** into allyl alcohols **7** were almost quantitative since the yields were similar starting either from the α-bromocarbonyl compounds **1** or from the isolated epichlorohydrins **3** (Table 3, entries 1 and 2).

Alternatively, the metallation with lithium powder of the epichlorohydrins **3** led to the same allyl alcohols **7**, after hydrolysis (Scheme 5 and Table 4). In this case, the chlorine-lithium exchange gave a β-functionalized organolithium compound which undergoes a spontaneous β-elimination yielding compounds **7**, after hydrolysis (Scheme 6).

Table 3. Synthesis of Substituted Allyl Alcohols **7** from α-Bromo or α-Chlorocarbonyl compounds **1** or **4**.

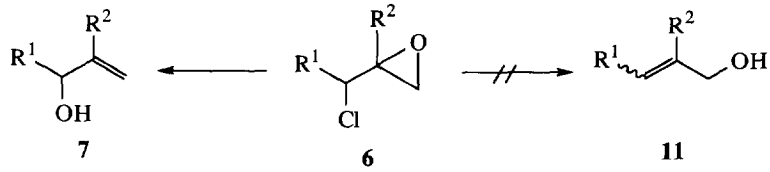
	α-Halocarbonyl Compound **1** or **4**					
Entry	Compound	R^1	R^2	Product	% Yield[a]	R_f[b]
1	**1a**	Me	Me	**7a**	71	0.48
2	**1a**	Me	Me	**7a**	70[c]	0.48
3	**4a**	Me	Me	**7a**	67	0.48
4	**4c**	n-Pr	H	**7b**	72	0.46
5	**4d**	i-Pr	H	**7c**	70	0.48
6	**1c**	n-Bu	H	**7d**	87	0.46
7	**4e**	n-Bu	H	**7d**	86	0.46
8	**1d**	n-Bu	n-Pr	**7e**	85[c]	0.47
9	**4f**	n-Bu	n-Pr	**7e**	79	0.47
10	**1e**	$n\text{-}C_6H_{13}$	H	**7f**	95	0.50

[a] Isolated yield based on the starting carbonyl compound **1** or **4**. [b]Hexane/ether : 3/2. [c]Epichlorohydrin **3** was used as starting material.



Scheme 6.

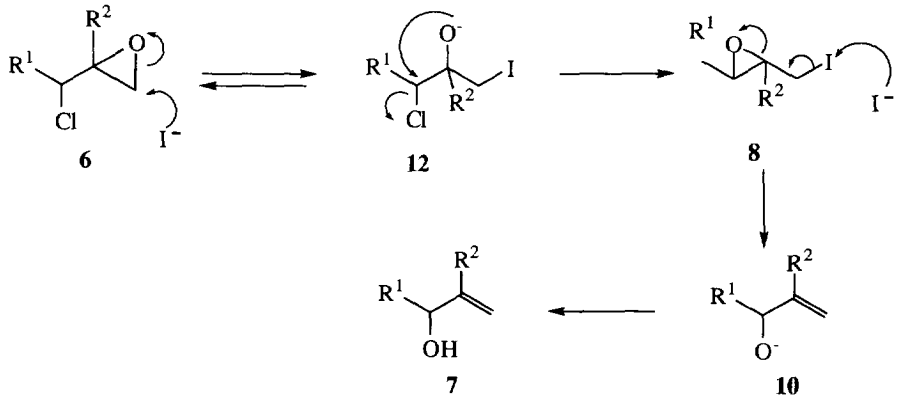
The same allyl alcohols **7** were prepared starting from α-chlorocarbonyl compounds **4** and iodomethyllithium in the presence of lithium iodide. The obtained alcohols **7** were the same as those prepared from α-bromocarbonyl compounds **1**; regioisomeric allyl alcohols **11** were never detected (Scheme 7).



7 **6** **11**

Scheme 7.

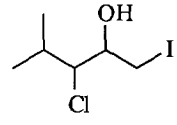
These results are consistent with the opening of the oxirane ring produced by attack of iodide leading to the dihalocompound **12**[24]. The further intramolecular displacement of the chlorine by oxygen affords the iodoepoxide **8**, which is the same intermediate as the one generated starting from α-bromocarbonyl compounds **1**. A similar halophilic attack of a second iodide induces a β-elimination reaction with opening of the oxirane ring yielding, after hydrolysis, the allyl alcohol **7** (Scheme 8). A similar opening of epoxides with different nucleophiles have been described[24]. So, the transformation of the epichlorohydrins into allyl alcohols by reaction with iodide can be produced by two different mechanisms. Depending on the steric hindrance, the iodide attacks to chlorine or to epoxide ring.



6 **12** **8** **7** **10**

Scheme 8.

This mechanism has been confirmed by isolation of compound **15** from an aliquot taken during the reaction process starting from **6d**. The NMR analysis (300 MHz) showed the presence of only one diastereoisomer, which its stereochemistry was not assigned.



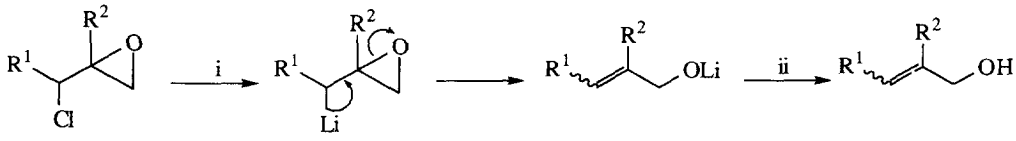
15

The transformation of epichlorohydrins **6** into substituted allyl alcohols by metallation with lithium powder was also carried out. In this case, the regioisomeric allyl alcohols **11** were isolated as a mixture of *Z/E* diastereoisomers (Scheme 9 and Table 4).

Table 4. Synthesis of Substituted Allyl Alcohols **7** and **11** by Reaction of Epichlorohydrins **3** or **6** with Lithium.

	Epichlorohydrin **3** or **6**						
Entry	Compound	R^1	R^2	Product	% Yield[a]	Diastereomeric excess[b]	R_f[c]
1	**3a**	Me	Me	**7a**	58	-	0.48
2	**3c**	n-Bu	H	**7d**	68	-	0.46
3	**3d**	n-Bu	n-Pr	**7e**	70	-	0.47
4	**6a**	Me	Me	**11a**	50	5	0.37
5	**6c**	n-Pr	H	**11b**	85	33	0.35[d]
6	**6d**	i-Pr	H	**11c**	40	60	0.45[e]
7	**6e**	n-Bu	H	**11d**	70	40	0.53[f]
8	**6f**	n-Bu	n-Pr	**11e**	80	33	0.38
9	**6g**	$-(CH_2)_3-$		**11f**	45	-	0.47
10	**6h**	$-(CH_2)_4-$		**11g**	61	-	0.45

[a] Isolated yield based on the starting epichlorohydrin. Calculated from ^1H and ^{13}C-NMR data. [c]Hexane/ether : 3/2. [d]Hexane/ether : 1/1. [e]Hexane/ether : 2/3. [f]Hexane/ether : 7/3.



6 **13** **14** **11**

Scheme 9. *Reagents and conditions*: i, Li, -78 to 20°C; ii, HCl-H_2O.

In the case of the epichlorohydrins **6a** and **6f** the synthesis of the *Z/E* mixture of allyl alcohols starting from only one diastereoisomer involves a partial inversion of the configuration at the anionic carbon atom prior to the β-elimination process, a stereospecific elimination being assumed.

EXPERIMENTAL

General. - TLC was carried out on Merck 60F-254 precoated silica gel on aluminium sheets. IR spectra were determined with a Perkin-Elmer 1720-XFT and Unicam Matlson 3000 FT spectrometers. ^1H and ^{13}C-NMR spectra were recorded on a Bruker AC-200 and Bruker AC-300; 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 5988 A spectrometer. Elemental analysis was carried out with a Perkin-Elmer 240 Elemental Analyser. Starting 3-chloro-2-butanone, 2-chlorocyclopentanone, 2-chlorocyclohexanone, diiodomethane, chloroiodomethane, methyllithium, lithium bromide, lithium iodide and lithium powder were of the best commercial grade available (Aldrich) and were used without further purification. α-Chloroaldehydes[25], α-bromoaldehydes[26], and α-chloro or α-

bromoketones[27] were prepared according to literature methods. Solvents were dried before as usually. All reactions were carried out under nitrogen and glassware was dried before use.

Preparation of Epichlorhydrins **3**. *General Procedure.* - To a stirred solution of the starting α-bromocarbonyl compound **1** (5 mmol), chloroiodomethane (11 mmol; 0.80 mL) and LiBr (11 mmol; 0.95 g) in THF (15 mL) was dropwise added methyllithium (11 mmol; 7.33 mL of 1.5 M solution in diethyl ether) during 15 min at -78°C under nitrogen. Stirring was continued for 1h at the same temperature and them overnight allowing it to warm to room temperature. The mixture was hydrolysed with saturated aqueous NH_4Cl (4 mL), extracted with ether (3x5 mL) and the combined layers were dried (Na_2SO_4). The solvents were removed (15 Torr) yielding the expected crude products **3** (>96% purity, NMR). Yields and R_f values are included in Table 1; analytical and spectral data follow.

(u)-2-Chloromethyl-2,3-dimethyloxirane (**3a**): IR (film) 3053 (CH ring) cm^{-1}; ^{1}H-NMR ($CDCl_3$) 1.25 (d, 3H, *J*=5.5, CH_3CH), 1.3 (s, 3H, CH_3C), 2.95 (q, 1H, *J*=5.5, CH_3CH), 3.35, 3.45 (2d, 2H, *J*=11.3, CH_2Cl); NOE positive between the signal at 2.95 and the signals at 3.35 and 3.45; ^{13}C-NMR ($CDCl_3$) 13.6, 14.0 (2xCH_3), 50.6 (CH_2Cl), 58.9 (CHO), 59.3 (CO); MS, *m/z* 85 (M+ -Cl, 13%), 76 (10), 58 (52), 51 (10), 49 (21), 45 (63), 43 (100), 42 (16), 41 (61), 40 (14), 39 (66), 38 (14); Anal. Calcd. for C_5H_9ClO: C, 49.81; H, 7.52. Found C, 49.7; H, 7.7.

(u)-2-Chloromethyl-2-phenyl-3-methyloxirane (**3b**): IR (film) 3030 (CH ring) cm^{-1}; ^{1}H-NMR ($CDCl_3$) 1.0 (d, 3H, *J*=5.3, CH_3), 3.4 (q, 1H, *J*=5.3, CHO), 3.7, 4.0 (2d, 2H, *J*=11.8, CH_2Cl), 7.2-7.6 (m, 5H, C_6H_5); NOE positive between the signal at 3.4 and the signals at 3.7 and 4.0; ^{13}C-NMR ($CDCl_3$) 14.3 (CH_3), 49.7 (CH_2Cl), 59.9 (CHO), 64.3 (CO), 127.3, 128.0, 128.2, 135.0 (C_6H_5); MS, *m/z* 184 (M^+ +2, <1%), 182 (M^+, <1), 120 (12), 105 (28), 104 (19), 103 (100), 102 (25), 91 (11), 78 (14), 77 (78), 76 (17), 75 (15), 74 (18), 63 (30), 52 (10), 51 (68), 50 (39), 49 (32), 44 (13), 43 (80), 42 (13), 39 (21); Anal. Calcd. for $C_{10}H_{11}ClO$: C, 65.76; H, 6.07. Found C, 65.5; H, 6.2.

(u)-2-Butyl-3-chloromethyloxirane (**3c**): IR (film) 1263 (CO ring) cm-1; 1H-NMR ($CDCl_3$) 0.9 (t, 3H, *J*=7.3, CH_3), 1.3-1.6 (m, 6H, $CH_2CH_2CH_2$), 2.9 (dt, 1H, *J*=5.7 and 2.0, $CHCH_2$), 3.0 (dt, 1H, *J*=5.7 and 2.0, $CHCH_2Cl$), 3.5, 3.6 (2dd, 2H, *J*=12.0 and 5.2, CH_2Cl); NOE positive between the signal at 2.9 and the signals at 3.5 and 3.6; NOE negative between the signals at 2.9 and 3.0; ^{13}C-NMR ($CDCl_3$) 13.6 (CH_3), 22.1, 27.6, 30.8 ($CH_2CH_2CH_2$), 44.5 (CH_2Cl), 56.8 and 58.7 (2xCHO); MS, *m/z* 113 (M+ -Cl, 35%), 69 (100), 57 (35), 55 (18), 44 (14), 43 (25), 42 (14), 41 (48), 39 (25); Anal. Calcd. for $C_7H_{13}ClO$: C, 56.57; H, 8.82. Found C, 56.4; H, 9.0.

(u)-3-Butyl-2-chloromethyl-2-propyloxirane (**3d**): IR (film) 1259 (CO ring) cm-1; 1H-NMR ($CDCl_3$) 0.85, 0.9 (2t, 6H, *J*=7.3, 2xCH_3), 1.1-1.7 (m, 10H, $CH_2CH_2CH_2$ and CH_2CH_2), 2.8 (t, 1H, *J*=5.9, CHO), 3.3, 3.5 (2d, 2H, *J*=11.4, CH_2Cl); NOE positive between the signal at 2.8 and the signals at 3.3 and 3.5; ^{13}C-NMR ($CDCl_3$) 13.7, 14.0 (2xCH_3), 17.9, 22.2, 27.6, 28.4, 29.6, ($CH_2CH_2CH_2$ and CH_2CH_2), 48.2 (CH_2Cl), 61.8 (CO), 63.7 (CHO) ; MS, *m/z* 104 (M+ -$C_5H_{10}O$, <1%), 69 (14), 55 (11), 53 (11), 51 (12), 49 (12), 43 (30), 42 (21), 41 (100), 40 (16), 39 (78); Anal. Calcd. for $C_{10}H_{19}ClO$: C, 62.98; H, 10.04. Found C, 62.7; H, 10.2.

(u)-2-Chloromethyl-3-hexyloxirane (**3e**): IR (film) 1262 (CO ring) cm-1; 1H-NMR ($CDCl_3$) 0.85-0.9 (m, 3H, CH_3), 1.2-1.4 (m, 10H, $CH_2CH_2CH_2CH_2CH_2$), 2.9, 3.0 (2dt, 2H, *J*=5.6 and 2.1, 2xCHO), 3.5, 3.6 (2dd, 2H, *J*=11.4 and 5.6, CH_2Cl); 13C-NMR ($CDCl_3$) 13.9 (CH_3), 22,4, 28.8, 28.9, 31.3, 31.5 ($CH_2CH_2CH_2CH_2CH_2$), 44.5 (CH_2Cl), 57.0 and 59.0 (2xCHO); MS, *m/z* 141 (M+ -Cl, 2.5%), 97 (17), 79 (11), 69 (12), 57 (11), 55 (55), 53 (13), 49 (16), 43 (51), 42 (24), 41 (100), 40 (14), 39 (81); Anal. Calcd. for $C_9H_{17}ClO$: C, 61.18; H, 9.70. Found C, 61.0; H, 9.9.

Preparation of Epichlorohydrins **6**. *General Procedure.* - To a stirred solution of the starting α-chlorocarbonyl compound **4** (5 mmol) and diiodomethane (5 mmol; 0.40 mL) in THF (10 mL) was dropwise added methyllithium (5 mmol; 3.33 mL of 1.5 M solution in diethyl ether) during 5 min at -78°C under nitrogen. Then diiodomethane (5 mmol; 0.40 mL) and methyllithium (5 mmol; 3.33 mL of 1.5 M solution in diethyl ether) were again successively added. Stirring was continued for 15 min at the same temperature and for 1 h at 0°C. The mixture was hydrolysed with saturated aqueous NH_4Cl (4 mL), extracted with ether (3x5 mL) and the combined layers were dried (Na_2SO_4). The solvents were removed (15 Torr) yielding the expected crude products **6** (>96% purity, NMR). Yields, R_f values and diastereomeric excess are included in Table 2; analytical and spectral data follow.

2-(1-Chloroethyl)-2-methyloxirane (**6a**): IR (film) 3053 (CH ring) cm-1; 1H-NMR ($CDCl_3$) 1.3 (s, 3H, CH_3C), 1.5 (d, 3H, *J*=6.7, CH_3CH), 2.65, 2.7 (2d, 2H, *J*=4.8, CH_2O), 3.5 (q, 1H, *J*=6.7, CHCl); 13C-NMR ($CDCl_3$) 14.8, 20.1 (2xCH_3), 54.8 (CH_2O), 58.4 (CO), 60.4 (CHCl); MS, *m/z* 122 (M+ +2, <1%), 120 (M+, 2), 77 (10) 85 (26), 75 (17), 63 (18), 57 (23), 56 (56),

55 (100), 54 (16), 53 (35), 51 (17), 50 (14), 43 (81), 41 (15), 39 (44); Anal. Calcd. for C_5H_9ClO: C, 49.81; H, 7.52. Found C, 49.6; H, 7.8.

(u,l)-2-(1-Chloropropyl)oxirane (**6b**): IR (film) 3050 (CH ring) cm^{-1}; ^1H-NMR ($CDCl_3$) 1.01, 1.02 (2t, 3H, *J*=7.3, CH_3), 1.7-2.0 (m, 2H, CH_2CH_3), 2,6-2,7 (m, 1H, *H*CHO), 2.8-2.9 (m, 1H, *H*CHO), 3.0-3.1 (m, 1H, CHO), 3.3-3.4 (m, 1H, CHCl); ^{13}C-NMR ($CDCl_3$) 10.3, 10.8 (CH_3), 28.0, 29.0 (CH_2CH_3), 46.9 (CH_2O), 54.3, 55.0 (CHO), 63.7, 64.7 (CHCl); MS, *m/z* 120 (M^+, <1%), 107 (M^+ +2-CH_3, 12), 105 (M^+ -CH_3, 37), 92 (8), 90 (25), 75 (14), 55 (100), 54 (12), 43 (13), 41 (27), 40 (18), 39 (22); Anal. Calcd. for C_5H_9ClO: C, 49.81; H, 7.52. Found C, 49.7; H, 7.7.

(u,l)-2-(1-Chlorobutyl)oxirane (**6c**): IR (film) 3050 (CH ring) cm^{-1}; ^1H-NMR ($CDCl_3$) 0.89, 0.90 (2t, 3H, *J*=7.3, CH_3), 1.2-2.0 (m, 4H, CH_2CH_2), 2.6, 2.7 (2dd, 1H, *J*=2.5 and 4.7, *H*CHO), 2.8-2.9 (m, 1H, *H*CHO), 3.0, 3.1 (m, 1H, CHO), 3.4, 3.5 (2dt, 1H, *J*=4.3 and 8.2, CHCl); ^{13}C-NMR ($CDCl_3$) 13.4 (CH_3), 19.0, 19.2 (CH_2CH_3), 36.5, 37.7 (CH_2CHCl), 46.9 (CH_2O), 54.5, 55.1 (CHO), 61.9, 62.8 (CHCl); MS *m/z* 134 (M^+, <1%), 107 (M^+ +2-C_2H_5, 30), 105 (M^+ -C_2H_5, 100), 75 (11), 69 (11), 55 (14), 41 (19); Anal. Calcd. for $C_6H_{11}ClO$: C, 53.54; H, 8.24. Found C, 53.4; H, 8.4.

(u,l)-2-(1-Chloro-2-methylpropyl)oxirane (**6d**): IR (film) 3053 (CH ring) cm-1; ^1H-NMR ($CDCl_3$) 1.0-1.1 (m, 6H, 2xCH_3), 2.1-2.3 (m, 1H, $CHCH_3$), 2.65, 2.7 (2dd, 1H, *J*=4.9 and 2.5 *H*CHO), 2.9, 2.95 (2dd, 1H, *J*=4.9 and 3.9, HC*H*O), 3.1-3.2 (m, 1H, CHO), 3.3-3.4 (m, 1H, CHCl); ^{13}C-NMR ($CDCl_3$) 17.2, 18.4, 19.3, 19.4 (2xCH_3), 32.7, 33.1 ($CHCH_3$), 46.5, 47.5 (CH_2O), 52.7, 54.1 (CHO), 68.3, 70.0 (CHCl); MS, *m/z* 121 (M+ +2-CH_3, 4%), 119 (M+ -CH_3, 11), 75 (20), 69 (24), 63 (14), 61 (25), 57 (48), 55 (23), 53 (30), 51 (22), 50 (16), 49 (10), 43 (44), 42 (15), 41 (77), 40 (11), 39 (100), 38 (19); Anal. Calcd. for $C_6H_{11}ClO$: C, 53.54; H, 8.24. Found C, 53.4; H, 8.5.

(u,l)-2-(1-Chloropentyl)oxirane (**6e**): IR (film) 3050 (CH ring) cm-1; ^1H-NMR ($CDCl_3$) 0.9 (t, 3H, *J*=7.0, CH_3), 1.2-2.0 (m, 6H, $CH_2CH_2CH_2$), 2.7, 2.75 (2dd, 1H, *J*=4.8 and 2.5 *H*CHO), 2.9, 2.95 (2dd, 1H, *J*=4.8 and 3.9, *H*CHO), 3.1, 3.15 (2ddd, 1H, *J*=2.5, 3.9, and 7.8, CHO), 3.45, 3.55 (2dt, 1H, *J*=4.1 and 7.8, CHCl); ^{13}C-NMR ($CDCl_3$) 13.7 (CH_3), 22.0, 27.7, 35.4 ($CH_2CH_2CH_2$), 46.8 (CH_2O), 54.5 (CHO), 62.1 (CHCl); MS, *m/z* 107 (M+ +2 -C_2H_3O, 33%), 105 (M+ -C_2H_3O, 100), 92 (13), 69 (12), 67 (14), 56 (13), 55 (19), 53 (11), 43 (11), 41 (36), 39 (29); Anal. Calcd. for $C_7H_{13}ClO$: C, 56.57; H, 8.82. Found C, 56.3; H, 9.0.

2-(1-Chloropentyl)-2-propyloxirane (**6f**): IR (film) 3053 (CH ring) cm-1; ^1H-NMR ($CDCl_3$) 0.90, 0.91 (2t, 6H, *J*=7.3 and 7.0, 2xCH_3), 1.2-2.1 (m, 10H, $CH_2CH_2CH_2$ and CH_2CH_2), 2.6, 2.7 (2d, 2H, *J*=4.5, CH_2O), 3.45, (dd, 1H, *J*=4.5 and 4.8, CHCl); ^{13}C-NMR ($CDCl_3$) 13.7, 14.0 (2xCH_3), 17.0, 22.0, 28.6, 29.6, 33.5 ($CH_2CH_2CH_2$ and CH_2CH_2), 51.7 (CH_2O), 60.4 (CO), 66.3 (CHCl); MS, *m/z* 155 (M+ -Cl, 2%), 147 (23), 81 (12), 67 (10), 55 (17), 53 (18), 51 (13), 43 (39), 42 (20), 41 (100), 40 (12), 39 (73); Anal. Calcd. for $C_{10}H_{19}ClO$: C, 62.98; H, 10.04. Found C, 62.6; H, 10.2.

(u,l)-1-Oxa-4-chlorospiro [2,4] hepthane (**6g**): IR (film) 3048 (CH ring) cm-1; ^1H-NMR ($CDCl_3$) 1.6-2.4 (m, 6H, $CH_2CH_2CH_2$), 2.9, 3.0 (2d, 2H, *J*=5.1, CH_2O), 4.05, 4.1 (2d, 1H, *J*=5.3 and 4.9, CHCl); ^{13}C-NMR ($CDCl_3$) 20.0, 27.2, 34.3 ($CH_2CH_2CH_2$), 53.2 (CH_2O), 61.9 (CHCl), 64.6 (CO); MS, *m/z* 134 (M+ +2, <1%), 133 (10), 132 (M+, 2), 131 (29), 67 (100), 66 (16), 65 (18), 55 (32), 42 (12), 41 (30), 39 (36); Anal. Calcd. for C_6H_9ClO: C, 54.35; H, 6.84. Found C, 54.2; H, 7.0.

(u,l)-1-Oxa-4-chlorospiro [2,5] octhane (**6h**): IR (film) 3048 (CH ring) cm-1; ^1H-NMR ($CDCl_3$) 1.2-2.2 (m, 8H, $CH_2CH_2CH_2CH_2$), 2.7 (d, 1H, *J*=4.8, *H*CHO), 2.8 (dd, 1H, *J*=4.8, and 1.3, HC*H*O) 3.9, 3.95 (2d, 1H, *J*=6.0 and 4.1, CHCl); ^{13}C-NMR ($CDCl_3$) 19.6, 23.4, 28.3, 33.4 ($CH_2CH_2CH_2CH_2$), 53.5 (CH_2O), 58.9 (CO), 62.6 (CHCl); MS, *m/z* 81 (11%), 79 (20), 77 (15), 53 (24), 52 (13), 51 (34), 50 (21), 49 (15), 43 (31), 41 (45), 40 (14), 39 (100), 38 (21), 37 (10); Anal. Calcd. for $C_7H_{11}ClO$: C, 57.34; H, 7.56. Found C, 57.1; H, 7.7.

Synthesis of Allyl Alcohols **7** *by Means of Iodide. General Procedure.* - 1.5 M diethyl ether solution of methyllithium (11 mmol; 7.33 mL) was dropwise added to a stirred solution of chloroiodomethane (11 mmol; 0.80 mL), LiI (20 mmol; 2.70 g) and the corresponding α-bromocarbonyl compound **1** (5 mmol) in THF (15 mL) over 15 min at -78°C under nitrogen. Starting from α-chlorocarbonyl compounds **4** (5 mmol), a mixture of LiI (20 mmol; 2.70 g) and iodomethyllithium (10 mmol) was used and the generation of iodomethyllithium was the same described for the synthesis of **6** (see above). Stirring was continued for 1 h at the same temperature and then overnight allowing it to warm to room temperature. The reaction mixture was evaporated (0.1 Torr) at 50°C (bath temperature). The resulting residue was dissolved in ether (10 mL), hydrolysed with saturated aqueous NH_4Cl (4 mL), extracted with ether (3x5 mL) and washed with saturated aqueous $Na_2S_2O_3$ (3 mL). The ethereal layer was dried (Na_2SO_4) and the solvents were removed (15 Torr) yielding the expected crude products **7** (>96% purity, NMR). Yields and R_f values are included in

Table 3. Product **7b** was characterized by comparison with an authentic sample (Aldrich); analytical and spectral data of the other products **7** follow.

3-Methylbut-3-en-2-ol [28]**(7a)**: IR (film) 3427 (OH), 3075, 1650 (CH=C) cm-1; 1H-NMR ($CDCl_3$) 1.2 (d, 3H, *J*=6.5, CH_3CH), 1.7 (s, 3H, CH_3C), 1.75 (s, 1H, OH), 4.2 (q, 1H, *J*=6.5, CH), 4.7, 4.8 (2s, 2H, CH_2=C); 13C-NMR ($CDCl_3$) 17.5, 21.4 (2xCH_3), 71.0 (CH), 109.2 (CH_2=C), 148.6 (C=CH_2); MS, *m/z* 86 (M+, 9%), 71 (100), 45 (21), 43 (54), 41 (26), 39 (24).

4-Methylpent-1-en-3-ol **(7c)**: IR (film) 3361 (OH), 3052, 1717 (CH=C) cm-1; 1H-NMR ($CDCl_3$) 0.8-1.0 (m, 3H, CH_3), 1.2-1.3 (m, 3H, CH_3), 1.7-1.8 (m, 1H, $CHCH_3$), 2.6 (s, 1H, OH), 4.0-4.1 (m, 1H, CHOH), 5.1, 5.3 (2d, 2*H*, *J*=10.4 and 17.2, CH_2=CH), 5.9 (ddd, 1H, *J*=6.3, 10.4 and 17.2, CH=CH_2); 13C-NMR ($CDCl_3$) 15.1, 17.7 (2xCH_3), 33.4 ($CHCH_3$), 78.1 (CHOH), 115.5 (CH_2=CH), 139.3 (CH=CH_2); MS, *m/z* 100 (M+, <1%), 85 (8), 58 (19), 57 (100); Anal. Calcd. for $C_6H_{12}O$: C, 71.95; H, 12.08. Found C, 71.7; H, 12.2.

Hept-1-en-3-ol [29]**(7d)**: IR (film) 3384 (OH), 3079, 1645 (CH=C) cm-1; 1H-NMR ($CDCl_3$) 0.9 (t, 3H, *J*=6.7, CH_3), 1.2-1.6 (m, 6H, $CH_2CH_2CH_2$), 1.9 (s, 1H, OH), 4.1 (q, 1H, *J*=6.3, CHOH), 5.1, 5.2 (2d, 2*H*, *J*=10.4 and 17.2, CH_2=CH), 5.9 (ddd, 1H, *J*=6.3, 10.4 and 17.2, CH=CH_2); 13C-NMR ($CDCl_3$) 13.7 (CH_3), 22.3, 27.2, 36.4 (CH_2CH_2), 72.8 (CHOH), 114.0 (CH_2=CH), 141.1 (CH=CH_2); MS, *m/z* 114 (M+, <1%), 72 (19), 58 (14), 57 (100), 43 (11), 41 (16), 39 (14).

2-Propylhept-1-en-3-ol **(7e)**; IR (film) 3412 (OH), 3079, 1646 (CH=C) cm-1; 1H-NMR ($CDCl_3$) 0.8 (t, 6H, *J*=7.1, 2xCH_3), 1.1-1.6 (m, 9H, OH, CH_2CH_3 and $CH_2CH_2CH_2$), 1.95 (dd, 2H, *J*=7.3 and 7.6, CH_2C=CH_2), 4.0 (t, 1H, *J*=6.4, CH), 4.8, 4.9 (2s, 2H, CH_2=C); 13C-NMR ($CDCl_3$) 13.8 (2xCH_3), 20.9, 22.4, 27.7, 33.1, 34.9 (CH_2CH_2 and $CH_2CH_2CH_2$), 75.1 (CH), 108.8 (CH_2=C), 151.8 (C=CH_2); MS, *m/z* 156 (M+, <1%), 127 (10), 114 (10), 113 (40), 100 (20), 99 (100), 85 (11), 81 (14), 79 (15), 71 (70), 69 (16), 58 (11), 57 (30), 55 (17), 53 (10), 43 (35), 41 (42), 39 (22); Anal. Calcd. for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found C, 76.6; H, 13.0.

Non-1-en-3-ol [30]**(7f)**: IR (film) 3398 (OH), 3075, 1650 (CH=C) cm-1; 1H-NMR ($CDCl_3$) 0.7-0.9 (m, 3H, CH_3), 1.1-1.4 (m, 10H, $CH_2CH_2CH_2CH_2CH_2$), 1.4 (s, 1H, OH), 4.0-4.1 (m, 1H, CHOH), 5.0, 5.1 (2d, 2H, *J*=10.0 and 16.6, CH_2=CH), 5.7-5.9 (m, 1H, CH=CH_2); 13C-NMR ($CDCl_3$) 13.9 (2xCH_3), 22.4, 25.1, 29.1, 31.6, 36.8 ($CH_2CH_2CH_2CH_2CH_2$), 73.4 (CHOH), 114.3 (CH_2=CH), 141.1 (CH=CH_2); MS, *m/z* 124 (M+ -H_2O, <1%), 85 (15), 72 (18), 57 (100), 43 (25), 41 (30), 39 (20).

Synthesis of Allylic Alcohols **7** *and* **11** *by Lithiation. General Procedure.* - To a stirred solution of the corresponding epichlorohydrin **3** or **6** (5 mmol) in THF (10 mL) was added lithium powder (40 mmol; 0.28 g) at -78°C under nitrogen and the reaction was allowed to warm to room temperature overnight. Then the mixture was hydrolysed with H_2O and HCl aq, extracted with ether (3x5 mL) and the combined layers were dried (Na_2SO_4). The solvents were removed (15 Torr) yielding the expected allyl alcohols **7** or **11** (>96% purity, NMR). Yields and R_f values of products **7** are included in Table 4; for spectral data see above. Yields, R_f values and diastereomeric excess of **11** are included in Table 4. Product **11b** was characterized by comparison with an authentic sample (Aldrich); analytical and spectral data of the other products **11** follow.

(Z,E)-2-Methylbut-2-en-1-ol [31]**(11a)**: IR (film) 3404 (OH), 1645 (CH=C) cm-1; 1H-NMR ($CDCl_3$) 1.5-1.7 (m, 6H, 2xCH_3), 2.7 (s, 1H, OH), 3.9, 4.0 (2s, 2H, CH_2), 5.47, 5.50 (2q, 1H, *J*=6.5 and 6.9, CH); 13C-NMR ($CDCl_3$) 12.9, 13.2, 21.0 (CH_3), 61.0, 68.8 (CH_2OH), 120.4, 122.3 (CH=C), 134.9, 135.4 (C=CH); MS, *m/z* 86 (M+, 45%), 71 (100), 68 (23), 67 (26), 57 (12), 55 (11), 53 (26), 43 (32), 41 (24), 39 (19).

(Z,E)-4-Methylpent-2-en-1-ol [32]**(11c)**: IR (film) 3445 (OH), 1644 (CH=C) cm^{-1}; 1H-NMR ($CDCl_3$) 0.9 (d, 6H, *J*=6.7, 2xCH_3), 1.00, 1.05 (2d, 6H, *J*=6.7, 2xCH_3), 1.2 (s, 1H, OH), 2.1-2.3 (m, 1H, $CHCH_3$), 4.0-4.2 (2d, 2H, *J*=4.8 and 6.0, CH_2OH), 5.5-5.7 (m, 2H, CH=CH); 13C-NMR ($CDCl_3$) 22.1 (2xCH_3), 30.6 ($CHCH_3$), 63.7 (CH_2), 125.8 (CH=$CHCH_2OH$), 140.1 ($CHCH_2OH$); MS, *m/z* 100 (M^+, 4%), 96 (67), 93 (32), 92 (92), 91 (100), 90 (20), 81 (31), 69 (16), 67 (10), 57 (11), 55 (38), 53 (13), 43 (28), 41 (19), 40 (42), 39 (13).

(Z,E)-Hept-2-en-1-ol [33]**(11d)**: IR (film) 3472 (OH), 3013, 1712 (CH=C) cm^{-1}; 1H-NMR ($CDCl_3$) 0.8 (m, 3H, CH_3), 1.2-1.4 (m, 4H, $CH_2CH_2CH_3$), 1.7 (s, 1H, OH), 1.9-2.0 (m, 2H, CH_2CH=C), 4.0, 4.1 (2d, 2H, *J*=5.2 and 5.6, CH_2OH), 5.5-5.6 (m, 2H, 2xCH); 13C-NMR ($CDCl_3$) 13.7, 13.8 (CH_3), 22.0, 22.4 (CH_2CH_3), 26.9, 31.1 ($CH_2CH_2CH_3$), 31.6, 31.7 (CH_2CH), 58.1, 63.2 (CH_2OH), 128.4, 128.7 (CH=$CHCH_2OH$), 132.3, 132.8 ($CHCH_2OH$); MS, *m/z*, 114 (M^+, 6%), 96 (43), 85 (11), 83 (13), 81 (84), 71 (27), 70 (21), 68 (32), 67 (19), 57 (100), 55 (33), 54 (13), 44 (12), 43 (16), 41 (28), 39 (14).

(Z,E)-2-Propylhept-2-en-1-ol **(11e)**: IR (film) 3436 (OH), 3075, 1626 (CH=C) cm-1; 1H-NMR ($CDCl_3$) 0.7-1.0 (m, 6H, 2xCH_3), 1.1-1.4 (m, 7H, OH, $CH_2CH_2CH_3$ and CH_2CH_3), 1.9-2.0 (m, 4H, CH_2C=CH and CH_2CH=C), 3.9, 4.1 (2s, 2H, CH_2O), 5.2, 5.35 (2t, 1H, *J*=7.3, CH=C); 13C-NMR ($CDCl_3$) 13.8 and 14.0 (2xCH_3), 21.6, 22.1, 22.3, 22.4, 27.0, 28.6, 28.7,

29.8, 31.8, 32.1 ($CH_2CH_2CH_2$ and CH_2CH_2), 66.3, 66.9 (CH_2O), 126.6, 127.0 (*C*H=C), 138.0, 138.6 (*C*=CH); MS, *m/z* 156 (M+, 12), 113 (19), 109 (14), 99 (67), 96 (13), 95 (45), 83 (38), 82 (11), 81 (28), 79 (19), 77 (11), 71 (80), 70 (13), 69 (53), 68 (16), 67 (45), 65 (11), 57 (100), 56 (11), 55 (65), 53 (24), 43 (53), 41 (76), 39 (36); Anal. Calcd. for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found C, 76.7; H, 13.1.

1-(Cyclopentenyl)methanol [34] **(11f)**: IR (film) 3384 (OH), 1659 (CH=C) cm^{-1}; ^{1}H-NMR ($CDCl_3$) 1.8 (quintet, 2H, *J*=7.1, CH_2CH_2CH), 2.1-2.3 (m, 5H, OH and 2xCH_2C=), 4.1 (s, 2H, CH_2OH), 5.5-5.55 (m, 1H, CH=C); ^{13}C-NMR ($CDCl_3$) 23.3 (CH_2CH_2CH), 32.1, 32.4 (2xCH_2C=), 61.9 (CH_2OH), 125.2 (CH), 144 (C).

1-(Cyclohexenyl)methanol [31] **(11g)**: IR (film) 3343 (OH), 3050, 1670 (CH=C) cm-1; ^{1}H-NMR ($CDCl_3$) 1.5-1.7 (m, 5H, 2xCH_2CH_2C=C and OH), 1.95-2.0 (m, 4H, 2xCH_2C=C), 4.0 (s, 2H, CH_2O), 5.6-5.7 (m, 1H, CH=C); ^{13}C-NMR ($CDCl_3$) 22.1, 22.2, 24.6, 25.2 ($CH_2CH_2CH_2CH_2$), 66.7 (CH_2OH), 122.1 (*C*H=C), 137.1 (*C*=CH); MS, *m/z* 112 (M+, 9%), 81 (15), 79 (30), 77 (12), 55 (17), 53 (24), 52 (14), 51 (28), 50 (20), 42 (15), 41 (44), 40 (17), 39 (100), 38 (18).

3-Chloro-1-iodo-4-methylpentan-2-ol **(15)**: IR (film) 3424 (OH), 2964, 1076 (C-O) cm-1; ^{1}H-NMR ($CDCl_3$) 1.0, 1.05 (2d, 6H, *J*=6.7, 2xCH_3), 2.1 (sextet, 1H, *J*=6.7, *C*H(CH_3)$_2$), 3.3 (dd, 2H, *J*=1.9 and 6.0, CH_2I), 3.8 (dt, 1H, *J*=3.3 and 6.0, *C*HOH), 4.0 (dd, 1H, *J*=3.3 and 6.7, CHCl); ^{13}C-NMR ($CDCl_3$) 8.8 (CH_2I), 19.0, 20.1 (2xCH_3), 32.0 (*C*H(CH_3)$_2$), 71.3, 72.9 (CHO and CHCl); MS, *m/z* 264 (M+2, 2%), 262 (M+, 8), 171 (M+-C_4H_8Cl, 100), 91 ($C_4H_8Cl^+$, 12); Anal. Calcd. for $C_6H_{12}ClIO$: C, 27.45; H, 4.61. Found C, 27.1; H, 4.8[35].

REFERENCES AND NOTES

1. Chong, J.M.; *Tetrahedron Lett.* **1992**, *33*, 33-36.
2. Otera, J.; Matsuzaki, S. *Synthesis* **1986**, 1019-1020.
3. Johnson, F.; Panella, J. P.; Carlson, A. A. *J. Org. Chem.* **1962**, *27*, 2241-2243.
4. Iqbal, J.; Penedy, A.; Shukla, A.; Scrivastava, R. R.; Tripathi, S. *Tetrahedron* **1990**, *46*, 6423-6432.
5. a) Takano, S.; Yanase, M.; Sekiguchi, Y.; Ogasawara, K. *Tetrahedron Lett.* **1987**, *28*, 1783-1784. (b) Utimoto, K.; Lambert, C.; Fukuda, Y.; Shiragami, H.; Nozaki, H. *Tetrahedron Lett.* **1984**, *25*, 5423-5426.
6. De Camp Schuda, A.; Mazzocchi, P. H.; Fritz, G.; Morgan, T. *Synthesis* **1986**, 309-312.
7. a) Barluenga, J.; Llavona, L.; Bernad, P. L.; Concellón, J. M. *Tetrahedron Lett.* **1993**, *34*, 3173-3176. b) Barluenga, J.; Fernández-Simón, J. L.; Concellón, J. M.; Yus, M. *J. Chem. Soc., Chem. Commun.* **1988**, 536-537. c) Discordia, R. P.; Dittmer, D. C. *J. Org. Chem.* **1990**, *55*, 1414-1415. d) Polson, G.; Dittmer, D. C. *J. Org. Chem.* **1988**, *53*, 791-794. e) Yadav, J. S.; Shekharam, T.; Gadgil, V. R. *J. Chem. Soc., Chem Commun.* **1990**, 843-844.
8. Yadav, J. S.; Deshpande, P. K.; Sharma, G. V. M. *Tetrahedron* **1990**, *46*, 7033-7046.
9. For a review on Sharpless epoxidation see: Pfenninger, A. *Synthesis* **1986**, 89-116.
10. Substituted epichlorohydrins can be prepared in a multistep process: a) from allyl alcohols: Yadav, J. S.; Deshpande, P. K.; Sharma, G. V. M. *Tetrahedron Lett.* **1990**, *31*, 4495-4496. b) from 1,3-dichloro-2-propanone[7d].
11. Altenbach, H. J.: *Functional Group Transformation via Allyl Rearrangement* In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I.; Winterfeldt, E. Eds.; Pergamon Press: Oxford, 1991; vol. 6, pp. 829-873.
12. Barluenga, J.; Llavona, L.; Concellón, J. M.; Yus, M. *J. Chem. Soc, Perkin Trans. 1* **1991**, 297-300 and references cited therein.
13. Pretsch, E.; Clerc, T.; Seibl, J.; Simon, W. *Tabellen zur Strukturaufklärung Organischer Verbindungen mit Spektroskopischen Methoden*; Springer Verlag: Berlin, 1976.
14. Seebach, D.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 654-660.
15. a) Chérest, M.; Felkin, H.; Prudent, N. *Tetrahedron Lett.* **1968**, *47*, 2199-2204. b) Anh, N. T. *Top. Curr. Chem.* **1980**, *88*, 145-162.

16. Frenking, G.; Köhler, K. F.; Reetz, M. T. *Tetrahedron* **1991**, *47*, 8991-9004.
17. Bürgi, H. B.; Dunitz, J. D.; Shefter, E. *J. Am. Chem. Soc.* **1973**, *93*, 5065-5067.
18. Morrison, J. D.; Mosher, H. S. *Asymmetric Organic Reactions*, American Chemical Society: Washington, 1976; pp 117-127.
19. Kalinowski, H. O.; Berger, S.; Braun, S. *^{13}C-NMR Spectroscopie*; George Thieme Verlag: Suttgart, 1984.
20. Eliel, E. L.: *Application of Cram's Rule: Addition of Achiral Nucleophiles to Chiral Substrates*. In *Asymmetric Synthesis*; Morrison, J. D.; Academic Press: New York, 1983; Vol 2, Part A, pp 125-127.
21. a) Bartelett, P. A. *Tetrahedron* **1980**, *36*, 1-72. b) Yamamoto, Y.; Maruyama, K. *Heterocycles* **1982**, *18*, 357-386. c) Hikino, H.; Mohri, K.; Hikino, Y.; Arihara, S.; Takemoto, T.; Mori, H.; Shibata, K. *Tetrahedron* **1976**, *32*, 3015-3021. d) Reetz, M. T. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 556-569.
22. For a review on dimethylsulfoxium ylide, see: Gololobov, Y. G.; Nesmeyanov, A. N.; Lysenko, V. P.; Boldeskul, I. E. *Tetrahedron*, **1987**, *43*, 2609-2651.
23. Amouroux, R.; Ejjiyar, S. *Tetrahedron Lett.* **1991**, *32*, 3059-3062.
24. a) Lidy, W.; Sundermeyer, W. *Tetrahedron Lett.* **1973**, *14*, 1449-1452. b) Mullis, J. C.; Weber, W. P. *J. Org. Chem.* **1982**, *47*, 2873-2875. c) Blandy, C.; Choukroun, T. L.; Gervais,D. *Tetrahedron Lett.* **1983**, *24*, 4189-4192. d) Gassman, P. G.; Guggenheim, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 5849-5850. e) Gassman, P. G.; Gremban, R. S. *Tetrahedron Lett.* **1984**, *25*, 3259-3262. f) Babu Mereyala, H.; Frei, B. *Helv. Chim. Acta* **1986**, *69*, 415-418. g) Spessard, G. O.; Ritter, A. R.; Johnson, D. M.; Montgomery, A. M. *Tetrahedron Lett.* **1983**, *24*, 655-656. h) Sinou, D.; Emziane, M. *Tetrahedron Lett.* **1986**, *27*, 4423-4426.
25. Stevens, C. L.; Farkas, E.; Gillis, B. *J. Am. Chem. Soc.* **1954**, *76*, 2695-2698.
26. Bellesia, F.; Ghelfi, F.; Grandi, R.; Pagnoni, H. M. *J. Chem Res. (S)* **1986**, 428-429.
27. Barluenga, J.; Llavona, L.; Yus, M.; Concellón, J. M. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2890.
28. Hayashi, M.; Kaneko, T.; Oguni, N. *J. Chem. Soc., Perkin Trans. 1* **1991**, 25-28.
29. Midland, M. M.; Koops, R. W. *J. Org. Chem.* **1990**, *55*, 5058-5065.
30. Dittmer, D. C.; Discordia, R. P.; Zhang, Y.; Murphy, C. K.; Kumar, A.; Pepito, A. S.; Wang, Y. *J. Org. Chem.* **1993**, *58*, 718-731.
31. Bergens, S. H.; Noheda, P.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 2121-2128.
32. Wood, R. D.; Ganem, B. *Tetrahedron Lett.* **1982**, *23*, 707-710.
33. Wang, Z.; Zhou, W. *Tetrahedron* **1987**, *43*, 2935-2944.
34. Brown, J. B.; Henbest, H. B.; Jones, E. R. H. *J. Chem. Soc.* **1950**, 3634-3641.
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