Facile One-pot Transformation of Carboxylic Acid Chlorides into 2-Substituted Allyl Alcohols or Epichlorohydrins†

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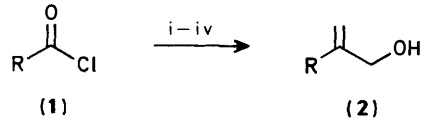
Treatment of carboxylic acid chlorides (**1**) with chloromethyl-lithium generated *in situ* (1 : 2 molar ratio) in the presence of lithium iodide leads, after hydrolysis, to the corresponding homologated 2-substituted allyl alcohols (**2**). When the same reaction is carried out using iodide-free butyl-lithium, instead of methyl-lithium–lithium iodide, the corresponding 2-substituted epichlorohydrins (**5**) are formed.

The allylation of carbonyl compounds to homoallylic alcohols using organometallic derivatives is an important synthetic operation.[1] However, the preparation of substituted systems presents the usual problems associated with regioselectivity in the allylic moiety and, consequently, they are relatively inaccessible.[2] On the other hand, the described chemistry of epichlorohydrins is practically concentrated on the simplest, chloromethyloxirane, due to its commercial usefulness in the preparation of polymers and highly cross-linked materials;[3] the corresponding substituted derivatives are much less well known. Recently, we[4] and others[5] have developed methodologies which permit the use of chloromethyl-lithium,[6] generated *in situ*,[7] in the preparation of epoxides or chlorohydrins,[5–7] terminal and exocyclic olefins,[4a] β-functionalized organolithium compounds and functionalized alcohols,[4b] and cyclopropanols,[4c] starting from carbonyl compounds. In the present paper, we report the one-pot transformation of carboxylic acid chlorides into 2-substituted allyl alcohols‡ or epichlorohydrins, using the same carbenoidic precursor.

Results and Discussion

The successive treatment of several carboxylic acid chlorides (**1**) with a mixture of chloroiodomethane–lithium bromide§ (1:2 molar ratio) and then with methyl-lithium–lithium iodide (1:2 molar ratio; prepared from methyl iodide and lithium) at −78 °C leads, after warming, evaporation under reduced pressure (essential), and hydrolysis, to the corresponding 2-substituted allyl alcohols (**2**) (Scheme 1, Table 1).

A stoicheiometric amount of iodine is obtained in this reaction, the suggested mechanism of which involves the intermediates (**3**)—(**6**) (Scheme 2). The formation of these intermediates is based on the following sequence: (i) after the first double addition of chloromethyl-lithium to the carboxylic acid chlorides (**1**) (2:1 molar ratio), hydrolysis leads to the corresponding dichlorohydrin (**3**);[4c] (ii) the transformation (**3**)→(**5**) has been proved by treatment with iodide-free butyl-lithium instead of methyl-lithium containing iodide: in this case the corresponding epichlorohydrin (**5**) was obtained (see below); the probable participation of intermediate (**4**) is possibly due to lithium iodide being in the reaction medium (arising from



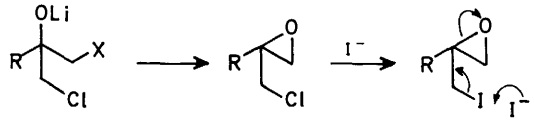
R
a; CH_2=C(Me)
b; MeCH=CH
c; c-C_3H_5
d; c-C_4H_7
e; Bu
f; Bu^i
g; Bu^t
h; Ph
i; c-C_6H_{11}

Scheme 1. *Reagents and conditions:* i, 2 $ClCH_2I$–LiBr; ii, 2 MeLi–LiI, −78 °C; iii, −78—25 °C, then evaporation; iv, NH_4Cl–water

Table 1. Substituted allylic alcohols (**2**) from carboxylic acid chlorides (**1**)

Carboxylic acid chloride (**1**)	Allylic alcohol (**2**) No.	% Yield[a]	B.p./°C (mmHg)
1a)	(**2a**)	57	50—54 (15)
(**1b**)[b]	(**2b**)[b]	60	53—57 (15)[b]
(**1c**)	(**2c**)	70	49—53 (15)
(**1d**)	(**2d**)	70	64—68 (15)
(**1e**)	(**2e**)	75	68—72 (15)[c]
(**1f**)	(**2f**)	70	65—69 (15)
(**1g**)	(**2g**)	45	61—65 (15)[d]
(**1h**)	(**2h**)	85	57—61 (0.01)[e]
(**1i**)	(**2i**)	88	60—63 (0.01)

[a] Isolated yields based on the starting carboxylic acid chloride (**1**). [b] The starting material (**1b**) and the obtained product (**2b**) are both *ca.* 95:5 *E*:*Z* isomeric mixtures (g.l.c. and n.m.r.). [c] Lit.,[8] b.p. 170—171 °C (760 mmHg). [d] Lit.,[8] b.p. 161—162 °C (760 mmHg). [e] Lit.,[9] b.p. 116—117 °C (11 mmHg).



Scheme 2.

† Preliminary communication, J. Barluenga, J. M. Concellón, J. L. Fernández-Simón, and M. Yus, *J. Chem. Soc., Chem. Commun.*, 1988, 536.

‡ Allyl alcohols are important starting materials for asymmetric epoxidation (see for instance: Y. Gao, R. M. Hanson, J. M. Klunder, S. Y. Ko, H. Masamune, and K. B. Sharpless, *J. Am. Chem. Soc.*, 1987, **109**, 5765).

§ In the absence of this salt, the reaction yields a mixture of products.

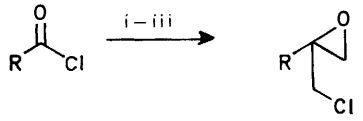
Table 2. Epichlorohydrins (**5**) from carboxylic acid chlorides (**1**)

Carboxylic acid chloride (**1**)	Epichlorohydrin (**5**) No.	% Yield[a]	B.p./°C (mmHg)
(**1a**)	(**5a**)	75	51—55 (15)
(**1b**)[b]	(**5b**)[b]	68	53—57 (15)
(**1c**)	(**5c**)	70	47—51 (15)
(**1d**)	(**5d**)	55	65—69 (15)
(**1e**)	(**5e**)	70	70—74 (15)
(**1f**)	(**5f**)	75	67—71 (15)
(**1g**)	(**5g**)	80	60—64 (15)
(**1h**)	(**5h**)	90	56—60 (0.01)[c]
(**1i**)	(**5i**)	70	61—62 (0.01)
(**1j**)	(**5j**)	60	85—88 (15)

[a] Isolated yield based on the starting carboxylic acid chloride (**1**). [b] The starting material (**1b**) and the obtained product (**5b**) are both *ca.* 95:5 *E*:*Z* isomeric mixtures (g.l.c. and n.m.r.). [c] Lit.,[13] 109—109.5 °C (6 mmHg).

methyl-lithium, prepared by treatment of methyl iodide with lithium) and the well known chlorine–iodine interchange reaction;[10] (iii) treatment of compound (**5**; R = H) with lithium iodide leads to a mixture of product (**6**; R = H) and 1,3-diiodopropan-2-ol (4:1) (by ^1H and ^{13}C n.m.r.); on the other hand, the presence of iodide rather than bromide results essentially in the transformation (**5**)→(**2**), since the treatment of the same starting material (**5**; R = H) with lithium bromide under the same reaction conditions does not yield the expected allyl alcohol (**2**); (iv) the iodide-induced β-elimination from 1,2-chloroiodo compounds which has already been described.[11] Taking these considerations into account, intermediate (**3**) is initially formed and then, either in this form or *via* the corresponding iodinated derivative (**4**), yields the epichlorohydrin (**5**); the chlorine–iodine exchange on compound (**5**) gives the iodo epoxide (**6**), which by treatment with iodide effects the epoxide* ring opening to yield, after hydrolysis, the allylic alcohol (**2**) (Scheme 2).

Epichlorohydrins were also prepared *via* the process (**1**)→(**5**) using iodide-free butyl-lithium in the same way as was described in Scheme 1. Thus, by successive treatment of carboxylic acid chlorides (**1**) with chloroiodomethane–lithium bromide (1:2 molar ratio) and then with iodide-free butyl-lithium (1:2 molar ratio; prepared from butyl chloride and lithium) at temperatures ranging between −78 and 20 °C, the expected substituted epichlorohydrins (**5**) were directly obtained (Scheme 3, Table 2).



(**1**) (**5**)

R

a; CH_2=C(Me)
b; MeCH=CH
c; c-C_3H_5
d; c-C_4H_7
e; Bu
f; Bu^i
g; Bu^t
h; Ph
i; c-C_6H_{11}
j; $Cl(CH_2)_4$

Scheme 3. *Reagents and conditions:* i, 2 $ClCH_2I$–LiBr; ii, 2 BuLi, −78—20 °C; iii, NH_4Cl–water

In conclusion, this paper describes a convenient, rapid, and versatile procedure for the synthesis of 2-substituted allylic alcohols and epichlorohydrins starting from readily available carboxylic acid chlorides.

Experimental

The experimental techniques and spectroscopic instrumentation used in the course of this work were as described in ref. 14.†

2-Substituted Allyl Alcohols (**2**). *General Procedure.*—A diethyl ether solution of methyl-lithium (1M, 11 mmol; prepared from methyl iodide and lithium)[15] was added to a stirred solution of chloroiodomethane (11 mmol), the starting carboxylic acid chloride (**1**) (5 mmol), and lithium bromide (11 mmol) in tetrahydrofuran (THF) (20 ml) over 15 min at −78 °C under argon. Stirring was continued for 1 h at the same temperature and then the solution was allowed to warm to room temperature. The reaction mixture was evaporated (0.1 mmHg) at 50 °C (bath temperature). The resulting residue was dissolved in hexane (10 ml) and hydrolysed with saturated aqueous NH_4Cl, extracted with diethyl ether, washed with saturated aqueous $Na_2S_2O_3$, the ethereal layer dried (Na_2SO_4), and evaporated (15 mmHg). The resulting residue was distilled *in vacuo* to afford the allylic alcohol (**2**).

3-Methyl-2-methylenebut-3-en-1-ol (**2a**) (Found: C, 73.0; H, 10.3. $C_6H_{10}O$ requires C, 73.43; H, 10.27%); $\nu_{max.}$(film) 3 330 (OH), 3 080, and 1 600 cm^{-1} (CH=C); $\delta_H(CDCl_3)$ 2.0 (4 H, s, Me, OH), 4.4 (2 H, s, CH_2O), and 5.0—5.5 (4 H, m, 2 × CH_2=C); $\delta_C(CCl_4)$ 21.8 (Me), 63.3 (CO), 112.5, 113.0 (2 × CH_2=C), 142.0, and 147.5 p.p.m. (2 × C=CH_2); *m/z* 98 (M^+, 100%), 97 (22), 83 (47), 80 (40), 79 (82), 77 (18), 70 (18), 69 (89), 67 (25), 65 (30), 57 (22), 56 (19), 55 (56), 53 (25), 52 (16), 51 (15), 43 (24), 42 (12), 41 (92), and 39 (53).

(*E*)-*2-Methylenepent-3-en-1-ol* (**2b**)‡ (Found: C, 73.1; H, 9.9. $C_6H_{10}O$ requires C, 73.43; H, 10.27%); $\nu_{max.}$(film) 3 370 (OH), 3 080, 3 020, and 1 610 cm^{-1} (CH=C); $\delta_H(CDCl_3)$ 1.6 (1 H, s, OH), 1.8 (3 H, d, *J* 5 Hz, Me), 4.3 (2 H, s, CH_2O), 4.9—5.2 (2 H, m, CH_2=C), and 5.5—6.1 (2 H, m, CH=CH); $\delta_C(CCl_4)$ 18.6 (Me), 62.9 (CO), 113.5 (CH_2=C), 125.3, 132.0 (CH=CH), and 145.5 p.p.m. (C=CH_2); *m/z* 98 (M^+, 53%), 83 (32), 80 (50), 79 (100), 77 (15), 69 (26), 67 (32), 65 (31), 55 (45), 53 (16), 43 (24), 42 (11), 41 (70), and 39 (38).

2-Cyclopropylprop-2-en-1-ol (**2c**) (Found: C, 73.1; H, 10.1. $C_6H_{10}O$ requires C, 73.43; H, 10.27%); $\nu_{max.}$(film) 3 400 (OH), 3 090, 3 070, and 1 640 cm^{-1} (ring CH_2, CH=C); $\delta_H(CDCl_3)$ 0.4—1.4 (5 H, m, 2 × ring CH_2, CH), 1.8 (1 H, s, OH), 4.1 (2 H, s, CH_2O), and 4.7—4.9 (2 H, m, CH_2=C); $\delta_C(CCl_4)$ 6.6 (2 × ring CH_2), 13.2 (CH), 65.0 (CH_2O), 105.8 (CH_2=C), and 151.1 p.p.m. (C=CH_2); *m/z* 98 (M^+, 26%), 83 (24), 80 (40), 79 (100), 77 (16), 69 (22), 67 (27), 65 (21), 57 (43), 55 (29), 53 (14), 51 (12), 43 (10), 41 (39), 39 (50), and 31 (18).

2-Cyclobutylprop-2-en-1-ol (**2d**) (Found: C, 75.1; H, 10.8. $C_7H_{12}O$ requires C, 74.95; H, 10.78%); $\nu_{max.}$(film) 3 350 (OH), 3 090, and 1 640 cm^{-1} (CH=C); $\delta_H(CDCl_3)$ 1.6 (1 H, s, OH), 1.7—2.4 (7 H, m, 3 × ring CH_2, CH), 4.0 (2 H, s, CH_2O), and 4.8—5.1 (2 H, m, CH_2=C); $\delta_C(CCl_4)$ 18.4, 27.8, 38.5 (3 × ring CH_2, CH), 63.9 (CO), 106.6 (CH_2=C), and 153.4 p.p.m. (C=CH_2); *m/z* 112 (M^+, 3%), 84 (100), 83 (85), 81 (12), 79 (20), 69 (21), 66 (10), 57 (15), 56 (62), 55 (98), 53 (21), 43 (12), 41 (26), and 39 (20).

* The transformation of epichlorohydrins into allylic alcohols by using telluride[2] or selenide[12] has been described.

† Whether CCl_4 was used as solvent for n.m.r. spectra or they were recorded as a neat sample, a D_2O capillary was employed as lock reference.

‡ The *Z* isomer (*ca.* 5%) is also present (g.l.c. and n.m.r.) (see footnote *b* in Table 1).

2-*Butylprop*-2-*en*-1-*ol* (**2e**);[8] $\nu_{max.}$(film) 3 350 (OH), 3 060, and 1 645 cm^{-1} (CH=C); $\delta_H(CDCl_3)$ 0.7—1.0 (3 H, m, Me), 1.2—1.5 (4 H, m, CH_2CH_2Me), 1.8 (1 H, s, OH), 1.9—2.1 (2 H, m, CH_2C=C), 4.0 (2 H, s, CH_2O), and 4.8—5.0 (2 H, m, CH_2=C); δ_C(neat) 14.4 (Me), 23.0, 30.5, 33.1 (3 × CH_2C), 66.2 (CH_2O), 109.8 (CH_2=C), and 150.1 p.p.m. (*C*=CH_2); *m/z* 114 (M^+, 9%), 81 (23), 72 (15), 71 (47), 68 (10), 58 (13), 57 (100), 55 (22), 43 (19), 41 (21), and 39 (13).

2-*Isobutylprop*-2-*en*-1-*ol* (**2f**) (Found: C, 73.4; H, 12.3. $C_7H_{14}O$ requires C, 73.63; H, 12.36%); $\nu_{max.}$(film) 3 390 (OH), 3 050, and 1 640 cm^{-1} (CH=C); $\delta_H(CDCl_3)$ 0.8 (6 H, d, *J* 5 Hz, 2 × Me), 1.2—1.8 (4 H, m, CH_2CH, OH), 4.0 (2 H, s, CH_2O), and 4.8—5.1 (2 H, m, CH_2=C); δ_C(neat) 22.0 (2 × Me), 26.1 (CH), 42.9 (CH_2CH), 65.0 (CH_2O), 110.3 (CH_2=C), and 148.5 p.p.m. (*C*=CH_2); *m/z* 114 (M^+, 3%), 96 (61), 81 (64), 79 (18), 72 (20), 71 (45), 70 (12), 67 (13), 57 (100), 56 (15), 55 (40), 54 (59), 53 (25), 51 (10), 43 (80), 42 (15), 41 (93), 40 (15), 39 (88), and 31 (25).

2-*t*-*Butylprop*-2-*en*-1-*ol* (**2g**);[8] $\nu_{max.}$(film) 3 360 (OH), 3 080, and 1 620 cm^{-1} (CH=C); $\delta_H(CDCl_3)$ 1.0 (9 H, s, 3 × Me), 1.5 (1 H, br signal, OH), 4.1 (2 H, s, CH_2O), and 4.8—5.0 (2 H, m, CH_2=C); $\delta_C(CCl_4)$ 29.5 (3 × Me), 34.8 (*C*Me), 62.4 (CO), 107.0 (CH_2=C), and 157.5 p.p.m. (*C*=CH_2); *m/z* 99 (M^+ − Me, 11%), 84 (12), 83 (100), 82 (10), 81 (82), 79 (71), 71 (11), 70 (27), 67 (14), 59 (43), 58 (43), 57 (85), 56 (14), 55 (65), 53 (29), 43 (17), 41 (52), and 39 (29).

2-*Phenylprop*-2-*en*-1-*ol* (**2h**);[9] $\nu_{max.}$(film) 3 350 (OH), 3 070, 3 050, 3 020, 1 625, 1 600, and 1 490 cm^{-1} (CH=C); $\delta_H(CDCl_3)$ 1.6 (1 H, s, OH), 4.5 (2 H, s, CH_2O), 5.3—5.5 (2 H, m, CH_2=C), and 7.3—7.5 (5 H, m, ArH); δ_C(neat) 64.2 (CH_2O), 112.3 (CH_2=C), 127.3, 128.5, 129.6, 139.8 (ArC), and 148.2 p.p.m. (*C*=CH_2); *m/z* 154 (M^+, 66%), 133 (30), 115 (22), 105 (58), 104 (22), 103 (100), 102 (22), 92 (44), 91 (43), 79 (23), 78 (47), 77 (81), 76 (12), 63 (14), 51 (38), 50 (22), and 39 (11).

2-*Cyclohexylprop*-2-*en*-1-*ol* (**2i**) (Found: C, 77.0; H, 11.5. $C_9H_{16}O$ requires C, 77.09; H, 11.50%); $\nu_{max.}$(film) 3 350 (OH), 3 080, and 1 640 cm^{-1} (CH=C); $\delta_H(CDCl_3)$ 1.0—1.8 (11 H, m, 5 × ring CH_2, CH), 1.6 (1 H, s, OH), 4.1 (2 H, s, CH_2O), and 4.8—5.0 (2 H, m, CH_2=C); $\delta_C(CCl_4)$ 26.7, 27.0, 32.8 (5 × ring CH_2), 41.4 (CH), 64.9 (CH_2O), 107.6 (CH=C), and 155.0 p.p.m. (*C*=CH_2); *m/z* 140 (M^+, 6%), 122 (25), 109 (34), 107 (25), 99 (28), 97 (14), 96 (26), 94 (19), 93 (25), 91 (12), 83 (48), 82 (26), 81 (77), 80 (22), 79 (52), 77 (20), 69 (10), 68 (16), 67 (100), 65 (12), 58 (27), 56 (20), 55 (73), 54 (17), 53 (22), 43 (12), 41 (47), 39 (34), and 31 (10).

2-*Substituted Epichlorohydrins* (**5**). *General Procedure*.—A diethyl ether solution of butyl-lithium (1M, 11 mmol; prepared from butyl chloride and lithium) was added to a stirred solution of chloroiodomethane (11 mmol), the starting carboxylic acid choride (**1**) (5 mmol), and lithium bromide (11 mmol) in THF (20 ml) over 15 min at −78 °C under argon. Stirring was continued for 1 h at the same temperature and then the solution was allowed to warm to room temperature. The resulting mixture was then worked up as described above for compounds (**2**) yielding the corresponding products (**5**).

2-*Chloromethyl*-2-(*prop*-1-*en*-2-*yl*)*oxirane* (**5a**) (Found: C, 54.1; H, 6.9. C_6H_9ClO requires C, 54.35; H, 6.84%); $\nu_{max.}(CCl_4)$ 3 070, 3 050 (oxirane CH, CH=C), and 1 640 cm^{-1} (C=C); $\delta_H(CDCl_3)$ 1.7—1.9 (3 H, m, Me), 2.75, 2.9 (2 H, 2 d, *J* 5 Hz, CH_2Cl), 3.5—3.8 (2 H, m, CH_2O), and 5.0—5.3 (2 H, m, CH_2=C); $\delta_C(CCl_4)$ 19.4 (Me), 47.5, 54.0 (CH_2Cl, CH_2O), 61.0 (CO), 114.5 (CH_2=C), and 142.0 p.p.m. (*C*=CH_2); *m/z* 133 (M^+ + 1, 2%), 131 (M^+ − 1, 5), 104 (16), 102 (46), 97 (10), 83 (24), 68 (12), 67 (100), 66 (26), 65 (41), 55 (53), and 53 (33).

(E)-2-*Chloromethyl*-2-(*prop*-1-*enyl*)*oxirane* (**5b**)* (Found: C, 54.4; H, 7.0. C_6H_9ClO requires C, 54.35; H, 6.84%); $\nu_{max.}$(film) 3 070, 3 050 (oxirane CH, CH=C), and 1 640 cm^{-1} (C=C); $\delta_H(CDCl_3)$ 1.7 (3 H, d, *J* 5 Hz, Me), 2.75, 2.9 (2 H, 2 d, *J* 5 Hz, CH_2Cl), 3.5—3.7 (2 H, m, CH_2O), and 5.2—6.0 (2 H, m, CH=CH); δ_C(neat) 27.5 (Me), 47.2, 55.0, (CH_2Cl, CH_2O), 57.6 (CO), 127.5, and 129.8 p.p.m. (CH=CH); *m/z* 134 (M^+ + 2, <1%), 132 (M^+, 2), 119 (14), 117 (43), 83 (18), 81 (11), 68 (17), 67 (100), 66 (16), 65 (33), 55 (20), 53 (21), 51 (11), 43 (12), 41 (33), and 39 (32).

2-*Chloromethyl*-2-*cyclopropyloxirane* (**5c**) (Found: C, 54.4; H, 6.6. C_6H_9ClO requires C, 54.35; H, 6.84%); $\nu_{max.}$(film) 3 060 and 3 040 cm^{-1} (ring CH); $\delta_H(CDCl_3)$ 0.1—0.7 (4 H, m, ring CH_2CH_2), 1.2—1.7 (1 H, m, CH), 2.6, 2.75 (2 H, 2 d, *J* 5 Hz, CH_2Cl), and 3.5, 3.75 (2 H, 2 d, *J* 12 Hz, CH_2O); δ_C(neat) 1.5, 3.2 (ring CH_2CH_2), 12.3 (CH), 49.5, 52.7 (CH_2Cl, CH_2O), and 59.5 p.p.m. (CO); *m/z* 133 (M^+ + 1, 4%), 131 (M^+ − 1, 14), 97 (15), 83 (51), 68 (11), 67 (100), 66 (17), 65 (33), 55 (67), 53 (22), 51 (14), 49 (11), 41 (32), 40 (12), and 39 (46).

2-*Chloromethyl*-2-*cyclobutyloxirane* (**5d**) (Found: C, 57.1; H, 7.5. $C_7H_{11}ClO$ requires C, 57.34; H, 7.56%); $\nu_{max.}(CCl_4)$ 3 060 cm^{-1} (oxirane CH); $\delta_H(CDCl_3)$ 1.8—2.2 (7 H, m, 3 × ring CH_2, CH), 2.7 (2 H, s, CH_2Cl), and 3.3, 3.6 (2 H, 2 d, *J* 12 Hz, CH_2O); $\delta_C(CCl_4)$ 17.8, 22.0, 24.2 (3 × CH_2), 35.0 (CH), 46.7, 50.1 (CH_2Cl, CH_2O), and 59.3 p.p.m. (CO); *m/z* 147 (M^+ + 1, <1%), 145 (M^+ − 1, 2), 120 (34), 119 (11), 118 (100), 117 (14), 111 (13), 97 (42), 90 (18), 88 (54), 83 (26), 81 (29), 79 (54), 77 (38), 69 (98), 67 (64), 65 (13), 55 (26), 54 (27), 53 (80), 52 (19), 51 (22), 49 (11), 43 (11), 41 (39), and 39 (29).

2-*Butyl*-2-(*chloromethyl*)*oxirane* (**5e**) (Found: C, 56.6; H, 8.7. $C_7H_{13}ClO$ requires C, 56.57; H, 8.81%); $\nu_{max.}$(film) 3 050 cm^{-1} (oxirane CH); $\delta_H(CCl_4)$ 0.8—1.0 (3 H, m, Me), 1.2—1.7 [6 H, m, $(CH_2)_3CO$], 2.6 (2 H, s, CH_2Cl), and 3.25, 3.6 (2 H, 2 d, *J* 12 Hz, CH_2O); $\delta_C(CCl_4)$ 14.5 (Me), 23.4, 27.2, 31.8 [$(CH_2)_3$], 48.9, 52.8 (CH_2Cl, CH_2O), and 59.0 p.p.m. (CO); *m/z* 135 (M^+ + 2 − Me, <1%), 133 (M^+ − Me, 3), 121 (19), 119 (54), 108 (35), 106 (100), 99 (10), 79 (11), 77 (27), 55 (18), 43 (12), 42 (14), and 41 (14).

2-*Chloromethyl*-2-*isobutyloxirane* (**5f**) (Found: C, 56.2; H, 8.9. $C_7H_{13}ClO$ requires C, 56.57; H, 8.81%); $\nu_{max.}$(film) 3 040 cm^{-1} (oxirane CH); $\delta_H(CCl_4)$ 0.9 (6 H, 2 d, *J* 5 Hz, 2 × Me), 1.2—1.8 (3 H, m, CH_2CH), 2.6 (2 H, s, CH_2Cl), and 3.25, 3.55 (2 H, 2 d, *J* 12 Hz, CH_2O); δ_C(neat) 23.0, 23.5 (2 × Me), 25.3 (CH), 41.0 (CH_2CH), 48.5, 52.9 (CH_2Cl, CH_2O), and 58.0 p.p.m. (CO); *m/z* 135 (M^+ + 2 − Me, 15%), 133 (M^+ − Me, 47), 113 (20), 108 (33), 106 (100), 99 (30), 79 (14), 77 (35), 75 (16), 69 (11), 67 (11), 55 (16), 49 (10), 43 (33), 42 (17), 41 (35), and 39 (25).

2-*Chloromethyl*-2-*t*-*butyloxirane* (**5g**) (Found: C, 56.7; H, 8.8. $C_7H_{13}ClO$ requires C, 56.57; H, 8.81%); $\nu_{max.}(CCl_4)$ 3 060 cm^{-1} (oxirane CH); $\delta_H(CCl_4)$ 0.95 (9 H, s, 3 × Me), 2.7, 2.8 (2 H, 2 d, *J* 5 Hz, CH_2Cl), and 3.3, 3.95 (2 H, 2 d, *J* 12 Hz, CH_2O); $\delta_C(CCl_4)$ 26.3 (3 × Me), 33.3 (*C*Me), 45.1, 49.0 (CH_2Cl, CH_2O), and 62.6 p.p.m. (CO); *m/z* 135 (M^+ + 2 − Me, 17%), 133 (M^+ − Me, 53), 133 (12), 84 (20), 83 (100), 79 (10), 77 (22), 69 (34), 67 (33), 65 (10), 57 (34), 56 (13), 55 (43), 53 (10), 51 (10), 49 (11), 43 (25), 41 (53), and 39 (25).

2-*Chloromethyl*-2-*phenyloxirane* (**5h**);[13] $\nu_{max.}$(film) 3 060, 3 040 (oxirane CH, CH=C), 1 600, and 1 490 cm^{-1} (C=C); $\delta_H(CDCl_3)$ 2.85, 3.15 (2 H, 2 d, *J* 5 Hz, CH_2Cl), 3.75, 4.0 (2 H, 2 d, *J* 12 Hz, CH_2O), and 7.3—7.5 (5 H, m, ArH); δ_C(neat) 48.8, 56.0 (CH_2Cl, CH_2O), 59.6 (CO), 126.9, 128.8, 129.0, and 138.1 p.p.m. (ArC); *m/z* 170 (M^+ + 2, 2%), 168 (M^+, 8), 167 (17), 133 (19), 104 (59), 103 (100), 102 (12), 91 (39), 77 (33), and 51 (15).

2-*Chloromethyl*-2-*cyclohexyloxirane* (**5i**) (Found: C, 61.7; H, 8.4. $C_9H_{15}ClO$ requires C, 61.89; H, 8.65%); $\nu_{max.}$(film) 3 060 cm^{-1} (oxirane CH); $\delta_H(CCl_4)$ 0.7—2.1 [11 H, m, $(CH_2)_5$, CH], 2.55, 2.7 (2 H, 2 d, *J* 5 Hz, CH_2Cl), and 3.3, 3.7 (2 H, 2 d, *J* 12 Hz, CH_2O); δ_C(neat) 21.8, 27.7, 29.2 [$(CH_2)_5$], 38.9 (CH), 47.5, 50.3 (CH_2Cl, CH_2O), and 61.2 p.p.m. (CO); *m/z* 174 (M^+, <1%), 139 (23), 134 (12), 132 (35), 125 (99), 121 (34), 119 (100), 109 (49),

* The *Z* isomer (*ca.* 5%) is also present (g.l.c. and n.m.r.) (see footnote *b* in Table 2).

108 (18), 107 (32), 106 (20), 95 (28), 93 (51), 91 (21), 83 (11), 82 (10), 81 (32), 80 (12), 79 (58), 77 (24), 68 (14), 67 (79), 65 (14), 55 (35), 54 (10), 53 (21), 51 (11), 43 (19), 41 (31), and 39 (25).

2-(4-*Chlorobutyl*)-2-(*chloromethyl*)*oxirane* (**5j**) (Found: C, 45.9; H, 6.5. $C_7H_{12}Cl_2O$ requires C, 45.92; H, 6.61%); $\nu_{max.}(CCl_4)$ 3 050 cm^{-1} (oxirane CH); $\delta_H(CDCl_3)$ 1.2—2.0 [6 H, m, $(CH_2)_3CO$], 2.7 (2 H, s, $COCH_2Cl$), and 3.4—3.7 (4 H, m, CH_2O, $ClCH_2CH_2$); $\delta_C(CCl_4)$ 22.2, 31.1, 33.0 [$(CH_2)_3CO$], 44.8, 48.3, 52.6 (2 × CH_2Cl, CH_2O), and 58.8 p.p.m. (CO); *m/z* 167 (M^+ − Me, 1%), 133 (12), 121 (33), 119 (100), 108 (28), 106 (88), 81 (34), 79 (20), 77 (36), 75 (17), 67 (10), 55 (22), 53 (19), 51 (10), 49 (17), 43 (14), 42 (19), 41 (31), and 39 (23).

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