γ-Substituted Secondary Organoalkaline Compounds and their Chlorinated Precursors: Synthetic Applications

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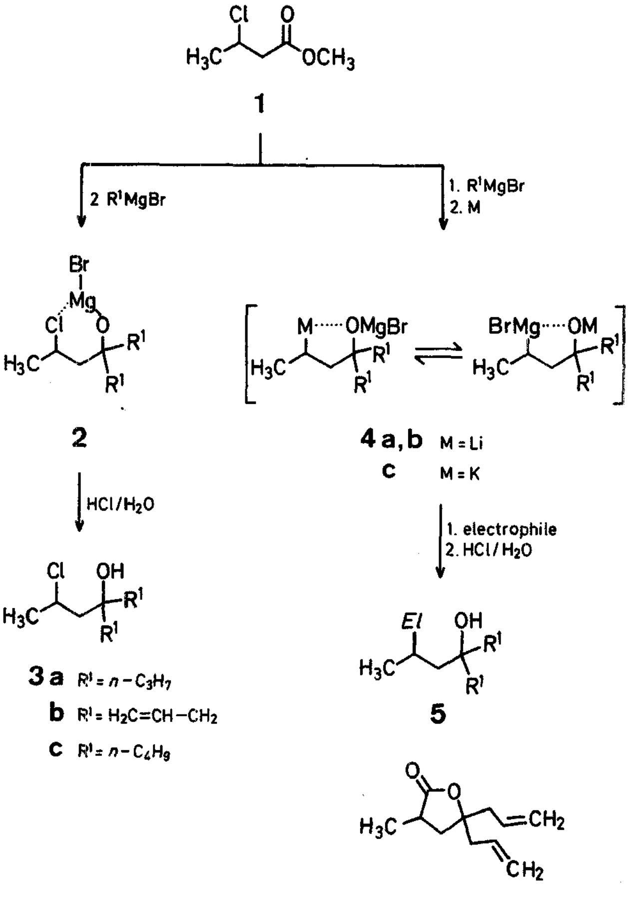
The preparation of γ-functionalised secondary organoalkaline metal compounds starting from methyl 3-chlorobutanoate (obtained by addition of hydrogen chloride to commercially available methyl *trans*-2-butenoate) is described. Reactions of these metallated compounds with suitable electrophilic reagents leads to a variety of tertiary alcohol derivatives.

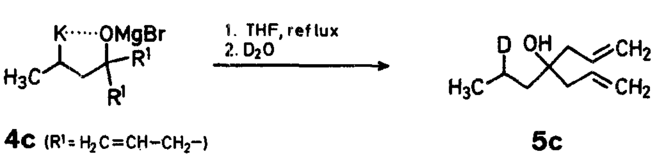
Recently, we reported the preparation of β-[1], γ-[2], and δ-substituted[3] organoalkaline compounds bearing the metal atom on a primary carbon atom starting from the corresponding chlorohydrins by direct metallation. The stability of these compounds depends on the relative positions of the functional group and metal atom: the β-functionalised systems are stable species only below $-78\,°C$ while the others can be prepared at room temperature. In the case of the β-functionalised organolithium compounds, the stability decreases when the metal is linked to a branched carbon atom: the secondary species are very unstable and decompose even at $-100\,°C$[1] by a β-elimination process yielding the corresponding olefins[4]. Here, we report on the behaviour of γ-functionalised organoalkaline compounds[5] with the metal linked to a secondary carbon atom, the behaviour of their precursors, the chlorohydrins, and their application for the synthesis of allylic alcohols.

When methyl 3-chlorobutanoate (**1**; obtained by addition of hydrogen chloride in ether to commercially available methyl *trans*-2-butenoate[6]) was allowed to react successively with a Grignard reagent and lithium powder, the corresponding γ-substituted organolithium compounds **4a,b** were obtained. The use of potassium[7] instead of lithium led to the corresponding intermediate **4c**. The initially obtained dimetallated derivatives **4** could also exist in equilibrium with the other isomeric structure with both the metal atoms interchanged (Scheme A). When the reaction mixture was hydrolysed after the first step of the process, the corresponding chlorohydrin **3** was isolated. The reaction of the synthons **4** with different electrophilic agents, such as water, deuterium oxide, dimethyl disulphide, oxygen, carbon dioxide, led to products **5**; in the case of the reaction with carbon dioxide, the lactone **5f** (R = allyl) was directly isolated.

The stability of the intermediate **4c** was tested by heating it in tetrahydrofuran solution for 2 h under reflux: subsequent deuteriolysis gave **5c** (~ 70% incorporation of deuterium from ^{13}C-N.M.R.) (Scheme **B**). No products resulting from elimination[1,2] or proton abstraction[2] were detected.



Scheme A



Scheme **B**

The preparation of the dilithium derivative **8** had to be carried out at $-78\,°C$ to avoid the decomposition of the chlorohydrin derivative **6**. Thus, when the first step of the reaction (addition of butyllithium to the chlorohydrin **3b**; R^1 = allyl) was performed at room temperature or at reflux (tetrahydrofuran) the product **7**, from a stereo- and regiospecific elimination of the intermediate **6**, was obtained[8]. The same process at $-78\,°C$ followed by metallation with lithium naphthalenide[9] led to the expected intermediate **8**, which reacted with dimethyl disulphide to afford the product **5d** (Scheme **C**).

Table 1. Products **3** and **5** prepared via Intermediates **2**, **4**, or **8**

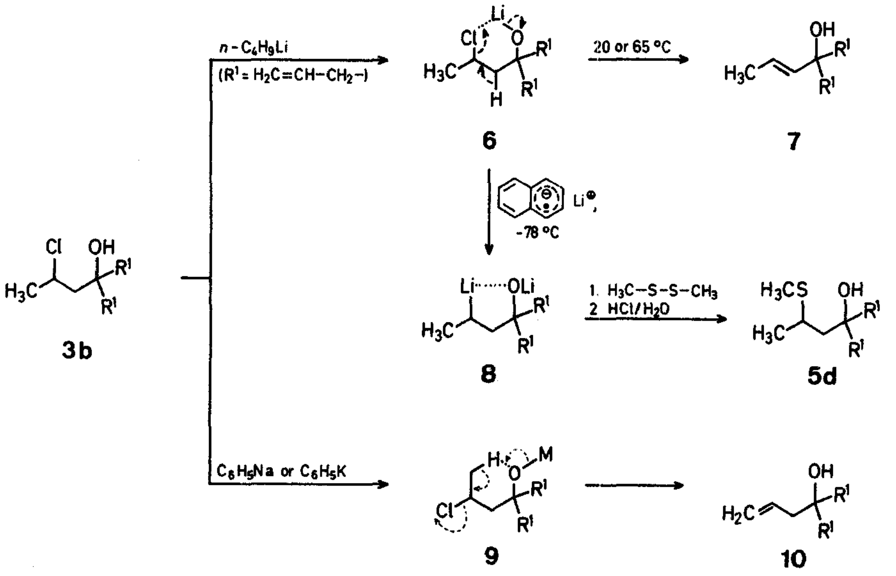
Product	Intermediate	R^1	M	electrophile [*El*]	Yield [%][a]	b.p. [°C]/ torr	Molecular Formula[b]
3a	**2a**	n-C_3H_7	–	–	43	109–111°/15	$C_{10}H_{21}ClO$ (192.7)
3b	**2b**	$H_2C{=}CH{-}CH_2{-}$	–	–	95	103–106°/15	$C_{10}H_{17}ClO$ (188.7)
3c	**2c**	n-C_4H_9	–	–	40	72–74°/0.1	$C_{12}H_{25}ClO$ (220.8)
5a	**4a**	n-C_3H_7	Li	$H_3C{-}S{-}S{-}CH_3[H_3C{-}S]$	36	92–95°/15	$C_{11}H_{24}OS$ (204.4)
5b	**4b**	$H_2C{=}CH{-}CH_2{-}$	Li	$H_2O[H]$	87	77–78°/15	$C_{10}H_{18}O$ (154.3)
5c	**4b**	$H_2C{=}CH{-}CH_2{-}$	Li	$D_2O[D]$	78	74–76°/15	$C_{10}H_{17}DO$ (155.3)
5c	**4c**	$H_2C{=}CH{-}CH_2{-}$	K	$D_2O[D]$	50 (40)[c]	–	–
5d	**4b**	$H_2C{=}CH{-}CH_2{-}$	Li	$H_3C{-}S{-}S{-}CH_3[H_3C{-}S]$	90	108–110°/0.1	$C_{11}H_{20}OS$ (200.3)
5d	**8**[d]	$H_2C{=}CH{-}CH_2{-}$	Li	$H_3C{-}S{-}S{-}CH_3[H_3C{-}S]$	30	–	–
5e	**4b**	$H_2C{=}CH{-}CH_2{-}$	Li	$O_2[OH]$	35	67–69°/0.001	$C_{10}H_{18}O_2$ (170.3)
5f	**4b**	$H_2C{=}CH{-}CH_2{-}$	Li	$CO_2[-]$	31	60–63°/0.1	$C_{11}H_{16}O_2$ (180.3)

[a] Yield of isolated product based on **1**.
[b] Satisfactory microanalyses obtained: C ±0.31, H ±0.09.
[c] The intermediate **4c** is heated under reflux in tetrahydrofuran.
[d] The intermediate **8** is prepared at −78 °C.

Table 2. Allylic Alcohols **7**, **10**, and **14** prepared

Product	Intermediate	R^1	M	Yield [%][a]	b.p. [°C]/torr	Molecular Formula[b] or Lit. b.p. [°C]/torr
7	**6**	–	–	25, (48)[c], (55)[d]	30–33°/0.1	$C_{10}H_{16}O$ (152.2)
10a	**9a**	n-C_3H_7	K	63	38–41°/0.1	no data given in Ref.[11]
10b	**9b'**	$H_2C{=}CH{-}CH_2{-}$	Na	62	38–40°/0.1	68–70°/8[12]
10b	**9b**	$H_2C{=}CH{-}CH_2{-}$	K	94		
10c	**9c**	n-C_4H_9	K	77	49–51°/0.1	$C_{12}H_{24}O$ (184.3)
14	**12**	–	–	48[e], (90)[f]	54–56°/15	50–51°/12[13]

[a] Yield of isolated product based on **3** or **11**.
[b] Satisfactory microanalyses obtained: C ±0.30, H ±0.12.
[c] Based on consumed starting material.
[d] The decomposition was carried out at 65 °C (tetrahydrofuran reflux).
[e] Only 1 mol of allylmagnesium bromide was used.
[f] Two mol of allylmagnesium bromide were used.



Scheme C

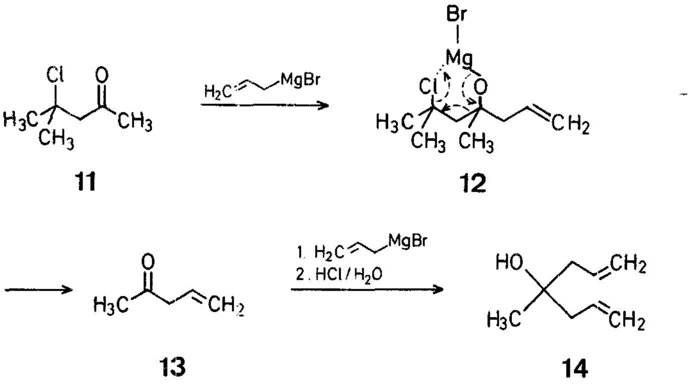
When the metal in the chlorohydrin salt was sodium or potassium (addition of phenylmetal to the chlorohydrin **3**), the corresponding intermediates **9** decomposed regioselectively to give the substituted allylcarbinols **10**. The different behaviour of the salts **6** and **9**, as shown by their decomposition products, can be explained considering steric hindrance: in the first case the small size of the lithium atom permits the formation of lithium chloride through a six-membered transition state; if the metal is sodium or potassium the larger size of the metal atom, together with the more anionic character of the oxygen-metal bond, leads to the intramolecular elimination process shown in Scheme C.

Table 3. Spectral Data for Compounds **3**, **5**, **7**, **10**, **11** and **14**

Product	I.R. (film)[a] ν [cm^{-1}]	^{1}H-N.M.R. (CCl_4/TMS)[b] δ [ppm]	^{13}C-N.M.R. (CCl_4)[b] δ [ppm][c]
3a	3460 (OH)	0.65–1.0 (m, 6H, $2C\underline{H}_3-CH_2$); 1.1–1.45 (m, 8H, $2C\underline{H}_2-C\underline{H}_2-CH_3$); 1.5 (d, 3H, $J = 6$ Hz, CH_3-C-Cl); 1.7–1.95 (m, 2H, CH_2-C-Cl); 2.45 (s, 1H, OH); 3,9–4.3 (m, 1H, CH)	14.4 (q, $2\underline{C}H_3-CH_2$); 16.4, 16.9 (2t, $2\underline{C}H_2-CH_3$); 27.3 (q, $\underline{C}H_3-CCl$); 40.7, 42.3 (2t, $2\underline{C}H_2C_2H_5$); 49.2 (t, $\underline{C}H_2-C-Cl$); 54.2 (d, CH); 73.7 (s, $C-O$)
3b	3430 (OH); 3040, 1640 ($CH=CH_2$)	1.6 (d, 3H, $J = 7$ Hz, CH_3); 1.8–2.0 (m, 2H, CH_2-C-Cl); 2.05 (s, 1H, OH); 2.3 (d, 4H, $J = 8$ Hz, $2CH_2-C=$); 4.05–4.5 (m, 1H, $CH-Cl$); 4.9–5.3 (m, 4H, $2CH_2=$); 5.5–6.15 (m, 2H, $2CH=$)	27.1 (q, CH_3); 43.7, 44.6 (2t, $2\underline{C}H_2-C=$); 48.8 (t, $\underline{C}H_2-C-Cl$); 53.7 (d, $CH-Cl$); 72.75 (s, $C-O$); 118.3, 118.5 (2t, $2CH_2=$); 133.3, 133.5 (2d, $2CH=$)
3c	3540 (OH)	0,75–1.1 (m, 6H, $2C\underline{H}_3-CH_2$); 1.2–1.5 [m, 12H, $2\ (C\underline{H}_2)_3-CH_3$]; 1.6 (d, 3H, $J = 6$ Hz, CH_3-C-Cl); 1.75–2.0 (m, 2H, CH_2-C-Cl); 2.05–2.5 (br. s, 1H, OH); 3.95–4.4 (m, 1H, CH)	13.9 (q, $2\underline{C}H_3-CH_2$); 23.2 (t, $2\underline{C}H_2-CH_3$); 25.5, 25.85 (2t, $2\underline{C}H_2C_2H_5$); 27.3 (q, $\underline{C}H_3-C-Cl$); 38.3, 39.7 (2t, $2\underline{C}H_2C_3H_7$-*n*); 49.2 (t, $\underline{C}H_2-C-Cl$); 54.3 (d, CH); 73.6 (s, $C-O$)
5a	3430 (OH)	0.75–1.15 (m, 6H, $2C\underline{H}_3-CH_2$); 1.15–1.8 [m, 13H, $2(C\underline{H}_2)_2-CH_3$, CH_2-C-S and CH_3-C-S]; 2.1 (s, 3H, CH_3-S); 2.55–3.05 (m, 2H, CH and OH)	12.0 (q, CH_3-S); 14.6 (q, $2\underline{C}H_3-CH_2$); 16.6, 17.0 (2t, $2\underline{C}H_2-CH_3$); 22.8 (q, $\underline{C}H_3-C-S$); 36.2 (d, CH); 41.9 (t, $2\underline{C}H_2C_2H_5$); 44.6 (t, $\underline{C}H_2-C-S$); 73.8 (s, $C-O$)
5b	3380 (OH); 3030, 1630 ($CH=CH_2$)	0.6–0.95 (deformed t, 3H, CH_3); 1.1–1.4 (m, 4H, $C\underline{H}_2-C\underline{H}_2-CH_3$); 1.85 (s, 1H, OH); 2.05 (d, 4H, $J = 8$ Hz, $2CH_2-C=$); 4.8–5.1 (m, 4H, $2CH_2=$); 5.45–6.1 (m, 2H, 2CH)[d]	14.3 (q, CH_3); 16.3 (t, $\underline{C}H_2-CH_3$); 41.6 (t, $\underline{C}H_2C_2H_5$); 43.8 (t, $2\underline{C}H_2-C=$); 73.2 (s, $C-O$); 117.3 (t, $2CH_2=$); 134.1 (d, 2CH)
5c	3380 (OH); 3040, 1635 ($CH=CH_2$)	0.7–1.0 (m, 3H, CH_3); 1.1–1.5 (m, 3H, CH_2-C-D and $CH-D$); 2.0 (s, 1H, OH); 2.1 (d, 4H, $J = 8$ Hz, $2CH_2-C=$); 4.8–5.1 (m, 4H, $2CH_2=$); 5.4–6.05 (m, 2H, $2CH=$)[d]	14.2 (q, CH_3); 15.9 (td, $J_{CD} = 19.3$ Hz, CHD); 41.5 (t, $\underline{C}H_2-C-D$); 43.8 (t, $2\underline{C}H_2-C=$); 73.2 (s, $C-O$); 117.3 (t, $2CH_2=$); 134.1 (d, $2CH=$)
5d	3420 (OH); 3035, 1635 ($CH=CH_2$)	1.25 (d, 3H, $J = 7$ Hz, CH_3-C); 1.45–1.65 (m, 2H, CH_2-C-S); 2.0 (s, 3H, CH_3-S); 2.1, 2.2 (2d, 4H, $J = 8$ Hz, $2CH_2-C=$); 2.55–3.0 (m, 2H, $CH-S$ and OH); 4.8–5.2 (m, 4H, $2CH_2=$); 5.5–6.05 (m, 2H, $2CH=$)[d]	12.2 (q, CH_3-S); 22.7 (q, $\underline{C}H_3-C$); 36.3 (d, $CH-S$); 44.3 (t, $2\underline{C}H_2-C=$ and $\underline{C}H_2-C-S$); 73.4 (s, $C-O$); 117.6, 117.8 (2t, $2CH_2=$); 134.1 (d, $2CH=$)
5e	3360 (OH); 3070, 1640 ($CH=CH_2$)[e]	1.1 (d, 3H, $J = 6$ Hz, CH_3); 1.4–1.65 (m, 2H, $C\underline{H}_2-C-CH_3$); 2.15, 2.35 (2d, 4H, $J = 8$ Hz, $2CH_2-C=$); 3.8 (s, 2H, 2OH); 3.95–4.45 (m, 1H, $CH-O$); 4.8–5.25 (m, 4H, $2CH_2=$); 5.4–6.25 (m, 2H, $2CH=$)	24.4 (q, CH_3); 43.05 (t, $\underline{C}H_2-C-CH_3$); 45.2 (t, $2\underline{C}H_2-C=$); 64.8 (d, $CH-O$); 74.4 (s, $C-O$); 117.75 (t, $2CH_2=$); 133.9, 134.2 (2d. $2CH=$)
5f	3060, 1650 ($CH=CH_2$); 1770 ($C=O$)	1.2 (d, 3H, $J = 7$ Hz, CH_3); 2.0–2.75 (m, 7H, $2CH_2-C=$ and $C\underline{H}_2-C\underline{H}-CH_3$); 4.8–5.3 (m, 4H, $2CH_2=$); 5.4–6.2 (m, 2H, $2CH=$)	15.5 (q, CH_3); 34.6 (d, $\underline{C}H-CH_3$); 37.75 (t, $\underline{C}H_2-C-CH_3$); 42.6, 43.7 (2t, $2\underline{C}H_2-C=$); 83.9 (s, $C-O$); 119.15, 119.2 (2t, $2CH_2=$); 132.1, 132.15 (2d, $2CH=$); 178.2 (s, $C=O$)
7	3450 (OH); 3070, 1650 ($CH=CH$)	1.75 (d, 3H, $J = 5$ Hz, CH_3); 1.8 (s, 1H, OH); 2.25 (d, 4H, $J = 8$ Hz, $2CH_2-C=$); 4.8–5.2 (m, 4H, $2CH_2=$); 5.3–6.1 (m, 4H, 4CH)	17.35 (q, CH_3); 45.1 (t, $2\underline{C}H_2-C=$); 73.2 (s, $C-O$); 117.6 (t, $2CH_2=$); 123.25 (d, $CH_3-\underline{C}H=$); 134.0 (d, $2\underline{C}H=CH_2$); 136.5 (d, $=\underline{C}H-C-O$)
10a	3400 (OH); 3040, 1640 ($CH=CH_2$)	0.75–1.1 (m, 6H, $2CH_3$); 1.15–1.55 (m, 8H, $2C\underline{H}_2-C\underline{H}_2-CH_3$); 2.15 (d, 2H, $J = 8$ Hz, $CH_2-C=$); 3.15 (br. s, 1H, OH); 4.8–5.2 (m, 2H, $CH_2=$); 5.4–6.1 (m, 1H, CH)	14.4 (q, $2\times CH_3$); 16.5 (t, $2\underline{C}H_2-CH_3$); 41.4 (t, $2\underline{C}H_2C_2H_5$); 43.8 (t, $\underline{C}H_2-C=$); 73.9 (s, $C-O$); 117.1 (t, $CH_2=$); 134.3 (d, CH)
10b	3420 (OH); 3030, 1650 ($CH=CH_2$)	2.2 (d, 6H, $J = 8$ Hz, $3CH_2-C=$); 2.4 (br. s, 1H, OH); 4.85–5.2 (m, 6H, $3CH_2=$); 5.5–6.15 (m, 3H, 3CH)	43.5 (t, $3\underline{C}H_2-C=$); 73.0 (s, $C-O$); 117.8 (t, $3CH_2=$); 133.8 (d, 3CH)
10c	3400 (OH); 3050, 1645 ($CH=CH_2$)	0.7–1.05 (m, 6H, $2CH_3$); 1.1–1.6 (m, 12H, $2C\underline{H}_2-C\underline{H}_2-C\underline{H}_2-CH_3$); 1.85 (br. s, 1H, OH); 2.15 (d, 2H, $J = 8$ Hz, $CH_2-C=$); 4.8–5.15 (m, 2H, $CH_2=$); 5.5–6.1 (m, 1H, CH)	13.8 (q, $2CH_3$); 23.2 (t, $2\underline{C}H_2-CH_3$); 25.4 (t, $2\underline{C}H_2C_2H_5$); 38.7 (t, $2\underline{C}H_2C_3H_7$-*n*); 43.8 (t, $\underline{C}H_2-C=$); 73.6 (s, $C-O$); 117.0 (t, $CH_2=$); 134.4 (d, CH)
11[f]	1720 ($C=O$)	1.7 (s, 6H, $2CH_3-C-Cl$); 2.15 (s, 3H, CH_3-C-O); 2.9 (s, 2H, CH_2)	31.4 (q, $\underline{C}H_3-C-O$); 32.1 (q, $2\underline{C}H_3-C-Cl$); 56.7 (t, CH_2); 66.8 (s, $C-Cl$); 193.6 (s, $C=O$)
14	3380 (OH); 3040, 1640 ($CH=CH_2$)	1.1 (s, 3H, CH_3); 2.15 (d, 4H, $J = 8$ Hz, $2CH_2-C=$); 2.6 (s, 1H, OH); 4.75–5.15 (m, 4H, $2CH_2=$); 5.5–6.1 (m, 2H, 2CH)	26.3 (q, CH_3); 46.1 (t, $2\underline{C}H_2-C=$); 71.6 (s, $C-O$); 117.4 (t, $2CH_2=$); 134.2 (d, 2CH)

[a] Recorded in a Pye Unicam SP-1025 I.R. spectrometer.
[b] Recorded in a Varian FT-80A spectrometer with a D_2O capillary.
[c] Refered to the solvent CCl_4.
[d] Recorded in a Varian EM-390 spectrometer.
[e] Recorded in a Perkin-Elmer 298 infrared spectrophotometer.
[f] 92% yield; b.p.: 41–44 °C/15 torr.

Finally, we investigated the possibility to prepare tertiary compounds derived from the chloroketone **11** (obtained by addition of hydrogen chloride in ether to commercially available mesityl oxide[6]). In this case, even the magnesium salt of the corresponding chlorohydrin **12** is unstable (compare with the intermediate **2**, Scheme **A**) and decomposes spontaneously to allyl methyl ketone (**13**)[10] which reacts with another molecule of allylmagnesium bromide to afford the product **14**. When the ketone/Grignard reagent molar ratio in this reaction is 1 : 2 the yield of **14** is 90% (Scheme **D**).



Scheme **D**

Chlorohydrins 3 via Intermediates 2; General Procedure:

A solution of methyl 3-chlorobutanoate (**1**; 2.7 g, 20 mmol) in tetrahydrofuran (20 ml) is added to a stirred ether solution of the corresponding Grignard reagent (44 mmol) under an argon atmosphere at −40 °C. The temperature is allowed to rise to 20 °C overnight, the mixture is then hydrolysed with water (15 ml) and neutralised (pH 7) with hydrochloric acid. The resultant mixture is extracted with ether (3 × 15 ml), the organic extract is washed with water (2 × 10 ml), dried with sodium sulphate, and evaporated at 15 torr. The residue is distilled in vacuo to afford the product **3** (Table 1).

Compounds 5 from Intermediates 4 and Electrophiles; General Procedure:

To a stirred mixture containing intermediate **2** (prepared as above) at −40 °C is added lithium powder or potassium[7] (60 mmol) and the temperature is allowed to rise to 20 °C overnight. The resulting suspension is filtered through a G-3 funnel. To the stirred filtrate, the electrophile (ratio of **4**/electrophile = 1/1) is added and stirring is continued for 2 h. The mixture is hydrolysed with water (20 ml) and worked up as described above to afford the products **5** (Table 1).

When oxygen is used as the electrophile[14] (*El* = OH) a stream of dry oxygen is bubbled through the solution of **4b** at −40 °C to 0 °C for 3 h and the mixture is then hydrolysed and worked up as described above.

The reaction with carbon dioxide as electrophile (*El* = COOH) is carried out by adding a precooled (−50 °C) solution of **4b** to excess anhydrous solid carbon dioxide. The resultant mixture is stirred for 4 h and then hydrolysed and worked up as described above.

4-(2-Methylthiopropyl)-1,6-heptadien-4-ol (5d) via Intermediate 8:

An ether solution of butyllithium (12 mmol) is added to a stirred solution of **3b** (1.9 g, 10 mmol) in tetrahydrofuran (20 ml) at −78 °C under an argon atmosphere. The mixture is stirred for 2 h, a tetrahydrofuran solution of lithium naphthalenide[1] (23 mmol) is then added, and stirring is continued for 7 h at −78 °C. Dimethyl disulphide (13 mmol) is added to the resultant mixture which is then stirred overnight while allowing the temperature to rise to 20 °C. The mixture is then hydrolysed and worked up as described above. Naphthalene is removed from the reaction residue by sublimation under reduced pressure (0.001 torr).

Alcohols 7, 10, and 14; General Procedure:

To a tetrahydrofuran solution of the chlorohydrin **3** or the chloroketone **11** (20 mmol) is added the corresponding organometallic compound (22 mmol of an ether solution of butyllithium, 22 mmol of phenylsodium[15] or phenylpotassium[15]; 22 or 44 mmol of an ether solution of allylmagnesium bromide[16]) at −40 °C and the mixture is stirred overnight while allowing the temperature to rise to 20 °C[16]. The resultant mixture is hydrolysed and worked up as described above to afford the products **7**, **10**, and **14** (Table 2).

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[8] The stereochemistry of the product **7** was confirmed by comparison of its spectral data with those of the same compound obtained by addition of allylmagnesium bromide to methyl crotonate and further hydrolysis.

[9] The lithiation with lithium powder at low temperature failed[1].

[10] The isobutene formed in the reaction was trapped by condensation of the reaction mixture before the final hydrolysis and mercuriation of the condensate with water/mercury(II) acetate; yield of 2-hydroxy-2-methylpropylmercury(II) acetate isolated: 46%.

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[16] See footnotes d, e and f in Table 2.