# sp²-Hybridized β-Substituted Organo-lithium, -sodium, and -potassium Dianions; Preparation, Stability, and Reactivity

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The reaction of the substituted 2-chloroallyl alcohol (3a) with ethylmagnesium bromide followed by lithium was found to give the β-substituted organolithium derivative (4) of the type C=CC(O). Intermediates of this type were also prepared directly from (E)-2-chlorocrotonaldehyde (2) or 2-chloro-acrolein (19) by the same process using different Grignard reagents. The use of sodium or potassium as the metal in the second step of the process was found to give the corresponding organosodium or organopotassium derivative (24) or (25). A dilithiated dianion (26) was also obtained from the corresponding chlorohydrin (3d) by reaction with phenyl-lithium followed by lithium. These intermediates, which are stable species at room temperature, were found to react stereoselectively with electrophilic reagents leading to functionalized substituted allyl alcohols. The thermal stability of the lithiated dianion (4d) has also been investigated.
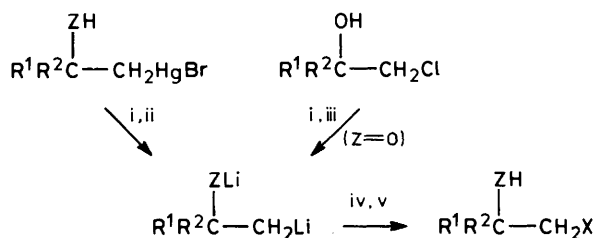
β-Substituted organometallic compounds derived from main group elements are difficult to prepare as they tend to undergo β-elimination reactions to give olefins.[1,2] For this reason, earlier attempts to synthesize intermediates of this type derived from magnesium [1,3] or lithium [4] gave only very low yields even at −100 °C. β-Substituted organometallics are more stable when the metal and the heteroatom are linked to an sp² hybridized carbon atom and are cis [5] to each other (see Scheme 1).

M = Li, MgHal
Y = Hal, OR, NR₂
Y′ = OR, NR₂
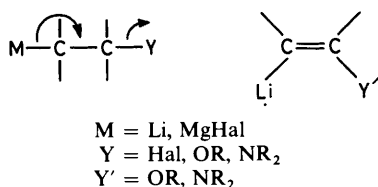
Scheme 1.

Recently, we reported two routes to β-substituted organo-lithium compounds at −78 °C: (a) by mercury–lithium trans-metallation of β-substituted organomercurials;[6] and (b) by direct lithiation with lithium naphthalenide of chlorohydrins.[7] These dianions are stable species at low temperature owing to the lowered electronegativity of the heteroatom at the β-position with respect to the metal atom.† The reactivity of these intermediates with electrophilic reagents has also been investigated [6,7] (Scheme 2).

We report here the direct preparation, stability, and reactivity

Scheme 2. *Reagents:* i, PhLi; ii, Li; iii, Li⁺C₁₀H₈⁻; iv, E = D₂O, RHal, O₂, CO₂, Me₂S₂, RCHO, R₂CO, RN=CR₂; v, HCl–H₂O

of the β-substituted organoalkaline ‡ compounds (4) in which the metal is linked to an sp²-hybridized carbon atom while the heteroatom is on an sp³-hybridized atom;§ they were prepared by a metallation process starting from the corresponding unsaturated chlorohydrins or aldehydes.

Results and Discussion

Successive treatment of the unsaturated chlorohydrin (3a) with ethylmagnesium bromide and lithium powder at −15 to 20 °C (Method A) led to the dianion (4a)‖ which by reaction with different electrophilic agents (D₂O, Me₂S₂, or CO₂) yielded stereoselectively the functionalized substituted allyl alcohols (5)—(7) (Scheme 3 and Table, entries 2, 4, 6).

The starting chlorohydrin (3a) was prepared by the addition of ethylmagnesium bromide to (E)-2-chlorocrotonaldehyde (2) [obtained by chlorination of *trans*-crotonaldehyde (1) with chlorine–sodium hydroxide¶] followed by hydrochloric acid hydrolysis (Scheme 3). The expected retention of configuration of the C–Li bond during the S_E reaction [8–11] [(4a)→(5)—(7)] was tested by comparison of the ¹H n.m.r. data (δ values for the olefinic protons) of compounds (5)—(7) with the calculated values.[12]

We have simplified and improved the above described method for dianionic intermediates of type (4)‖ starting directly from the 2-chloroaldehyde (2) by the addition of a Grignard reagent followed by lithium powder at −15 to 20 °C (Method B) (as described above). The resulting dianions (4) react with electrophiles (H₂O, D₂O, Me₂S₂, CO₂, Pr^iCHO, and HCONMe₂) to afford the corresponding substituted allyl alcohols (5)—(17) stereoselectively (Scheme 4 and Table, entries 1,3,5,7—13, and 17—19).

When the starting 2-chloro carbonyl compound is 2-chloro-acrolein (19) the corresponding β-substituted organolithium compounds (20)‖ were obtained; these react with electrophiles (D₂O, Me₂S₂) to give the expected substituted allyl alcohols (21)—(23) (Scheme 5 and Table, entries 20—22).

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‡ The term organoalkaline refers to organo-lithium, -sodium, and -potassium species.

§ The preparation of two intermediates of type (4) derivatives of primary alcohols, from the reaction of two unsaturated bromohydrins with s-[9] and t-butyl-lithium[9] at −78 °C, has been reported previously.

‖ The initially obtained dianions (4), (20), (24), and (25) exist in equilibrium with the isomeric structures in which the metal atoms are interchanged.

¶ For the stereochemistry of the addition–elimination reaction of halogen to substituted olefins see for instance ref. 8 and 10.

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† The stability of these intermediates could also be due to the formation of a ion pair, see A. Streitwieser, *J. Am. Chem. Soc.*, 1983, **105**, 2502, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1983, **105**, 7617.

Table. Preparation of the dianions (4), (20), and (24)—(26) and reaction with electrophiles (E)

Entry	Starting compound	Method[a]	Dianion	E	Product Yield (%)[b]	B.p. (°C/mmHg)
1	(2)	B	(4a)	D_2O	(5) 60	51—53/15
2	(3a)	A			78	
3	(2)	B	(4a)	Me_2S_2	(6) 45	52—54/0.1
4	(3a)	A			55	
5	(2)	B	(4a)	CO_2	(7)[c] 58[c]	64—66/0.1
6	(3a)	A			50[c]	
7	(2)	B	(4b)	D_2O	(8) 68	54—56/15
8	(2)	B	(4c)	H_2O	(9) 68	54—56/15
9	(2)	B	(4c)	D_2O	(10) 65	54—57/15
10	(2)	B	(4c)	Pr^iCHO	(11)[d] 52[d]	57—60/0.001
11	(2)	B	(4c)	$HCONMe_2$	(12) 48	68—70/0.1
12	(2)	B	(4d)	H_2O	(13) 79	64—66/15
13	(2)	B	(4d)	D_2O	(14) 70	64—67/15
14	(2)	B	(24)		55	
15	(2)	B	(25)		40	
16	(3d)	C	(26)		63	
17	(2)	B	(4d)	Me_2S_2	(15) 60	e
18	(2)	B	(4d)	CO_2	(16)[c] 67[c]	70—71/0.1
19	(2)	B	(4e)	D_2O	(17) 48	63—65/15
20	(19)	B	(20a)	D_2O	(21) 57	50—53/15
21	(19)	B	(20b)	D_2O	(22) 55	e
22	(19)	B	(20b)	Me_2S_2	(23) 48	53—55/0.1

[a] See Schemes 3—6. [b] Isolated yield based on starting compounds (2), (3a), and (19). [c] Isolated and characterized as its methyl ester (7') and (16') by treatment of the carboxylic acid with diazomethane. [d] Diastereoisomeric mixture (1.75:1, from g.l.c.). [e] This product was condensed trap-to-trap at 0.1 mmHg.
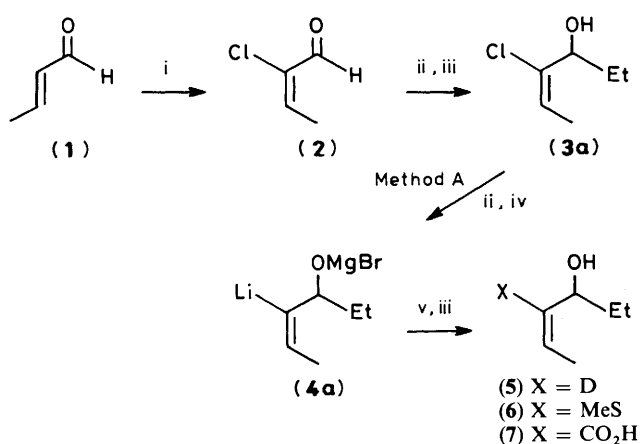
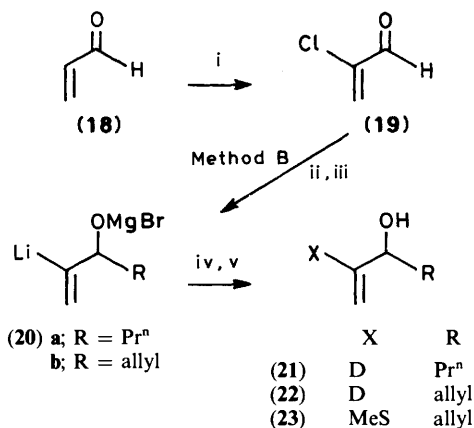**Scheme 3.** *Reagents:* i, Cl_2–NaOH; ii, EtMgBr; iii, $HCl-H_2O$; iv, Li; v, E = D_2O, Me_2S_2, CO_2
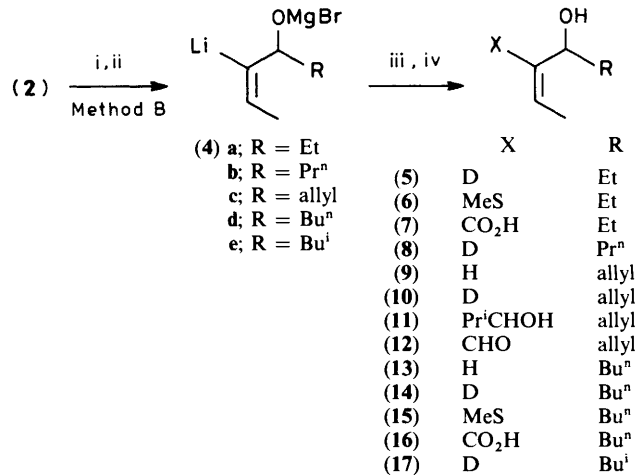
Scheme 4. *Reagents:* i, RMgBr; ii, Li; iii, E = H_2O, D_2O, Me_2S_2, CO_2, Pr^iCHO, $HCONMe_2$; iv, $HCl-H_2O$

We have also used Method B to obtain the corresponding β-substituted organosodium or organopotassium compounds. Thus, treatment of compound (2) with butylmagnesium bromide followed by lithium powder, sodium,* or potassium* under the same conditions as described above for intermediates (4) and (20) led to the dianions (4d), (24), and (25),† respectively. These organometallic compounds were characterized by deuteriolysis with deuterium oxide and conversion into the deuterio derivative (14) (Scheme 6 and Table, entries 13—15).

A dilithium derivative (26) was obtained by successive addition of phenyl-lithium and lithium (Method C) to the chlorohydrin (3d) [obtained by treatment of compound (2) with butylmagnesium bromide and further hydrolysis with hydrochloric acid]. The intermediate (26) was also characterized by deuteriolysis with deuterium oxide, and thus product (14) was isolated (Scheme 6 and Table, entry 16).

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* Sodium and potassium were used as metal plates prepared by dissolution of the metal in liquid ammonia at −50 °C followed by evaporation at 0.1 mmHg.
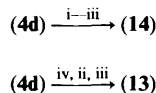
† The initially obtained dianions (4), (20), (24), and (25) exist in equilibrium with the isomeric structures in which the metal atoms are interchanged.

Scheme 5. *Reagents:* i, Cl_2–NaOH; ii, RMgBr; iii, Li; iv, E = D_2O, Me_2S_2; v, HCl–H_2O
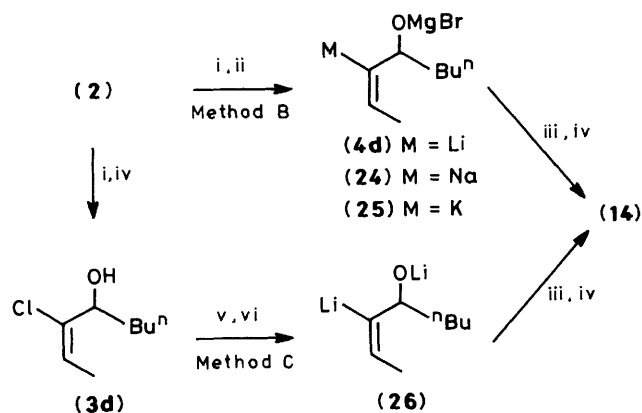
Scheme 6. *Reagents:* i, Bu^nMgBr; ii, M; iii, D_2O; iv HCl–H_2O; v, PhLi; vi, Li

$$(4d) \xrightarrow{\text{i--iii}} (14)$$

$$(4d) \xrightarrow{\text{iv, ii, iii}} (13)$$

Scheme 7. *Reagents and conditions:* i, THF, 65 °C; ii, D_2O; iii, HCl–H_2O; iv, dioxane, room temp.

Finally, we have investigated the thermal stability of the lithiated dianion (4d). When a tetrahydrofuran solution of (4d) was refluxed for 2 h and then treated with deuterium oxide, compound (14) was isolated; however, treatment of compound (4d) in dioxane (a better proton source than THF) at room temperature for the same period followed by further deuteriolysis led to the alcohol (13) as a result of proton abstraction from the reaction medium. The corresponding cumulene, which might have been expected from a β-elimination process,[1,2] was in no case isolated (Scheme 7).

The chemistry described in this paper offers a new route to the synthon C=CC(O̅).

Experimental

General.—I.r. spectra were determined with a Pye-Unicam SP-1000 spectrometer and recorded for films. ^1H and ^{13}C

N.m.r. spectra were recorded on a Varian FT-80 spectrometer, with $SiMe_4$ as internal standard; carbon tetrachloride was used as solvent and a D_2O capillary was employed as lock reference. The purity of the volatile distilled products was determined with a g.l.c. Varian Aerograph 2800 instrument equipped with an OV-101 Chromosorb column. Elemental analysis was carried out with a Perkin-Elmer 240 Elemental Analyser. Ether refers to diethyl ether. 2-Chlorocrotonaldehyde (2)[13] and 2-chloroacrolein (19)[14] were obtained from the corresponding aldehyde (Fluka, Merck) by the literature method.[15] The electrophilic reagents (E) were of the best commericial grade available (Aldrich, Fluka, and Merck) and were used without further purification. Grignard reagents and phenyl-lithium were prepared in ether by treating the corresponding bromo derivative with magnesium (turnings, Merck) or lithium (powder, <20μm, Kock Light) according to the standard methods[16] and used as *ca.* 1M-solutions. Sodium and potassium were used as metal plates (see Discussion). Ether was dried successively with anhydrous calcium chloride, sodium sulphate, sodium, and finally a K–Na (K_3Na) liquid alloy[17] under reflux, and was distilled and stored under argon. Tetrahydrofuran (THF) was dried successively with anhydrous calcium chloride and sodium sulphate; it was then refluxed with potassium, distilled, and stored under argon. Dioxane was dried successively with anhydrous calcium chloride and sodium sulphate, and finallly refluxed with sodium, distilled, and stored under argon. All reactions were carried out under argon and all glassware was dried before use.

Preparation of Chlorohydrins (3).—An ether solution of a Grignard reagent (16 mmol) was added to a stirred solution of 2-chlorocrotonaldehyde (2) (15 mmol) in THF (30 ml) at −15 °C under argon. The reaction mixture was stirred for 2 h and the temperature allowed to rise to 20 °C; the solution was then hydrolysed with water and neutralized with hydrochloric acid. The resulting solution was extracted with ether, and the organic layer washed with water and dried (Na_2SO_4). The solvents were removed (15 mmHg) and the resulting residue was distilled to afford the products (3a) and (3d). (E)-4-*Chlorohex-4-en-3-ol* (3a) [81% yield based on aldehyde (2)], b.p. 45—48 °C (0.1 mmHg) (Found: C, 53.4; H, 8.3. $C_6H_{11}ClO$ requires C, 53.54; H, 8.24%); $v_{max.}$ 3 400 cm^{-1} (OH); δ_H 0.9 (3 H, t, J 8 Hz, CH_3CH_2), 1.4—1.9 (5 H, m, with d at δ 1.8, J 6 Hz, CH_2CO and $CH_3C=C$), 3.8 (1 H, s, OH), 4.0 (1 H, t, J 6 Hz, CHO), and 5.75 (1 H, q, J 6 Hz, CH=C); δ_C 9.4 (q, CH_3CH_2), 13.1 (q, $CH_3C=C$), 27.3 (t, CH_2), 76.4 (d, CHO), 121.7 (d, $CH=C$), and 137.3 (s, CCl).

(E)-3-*Chloro-oct-2-en-4-ol* (3d) [88% yield based on aldehyde (2)], b.p. 66—68 °C (0.1 mmHg) (Found: C, 59.1; H, 9.4. $C_8H_{15}ClO$ requires C, 59.07; H, 9.30%); $v_{max.}$ 3 400 cm^{-1} (OH); δ_H 0.7—1.05 (3 H, m, CH_3CH_2), 1.1—1.55 (6 H, m, 3 × CH_2), 1.75 (3 H, d, J 6 Hz, CH_3CH), 3.65 (1 H, s, OH), 4.0 (1 H, t, J 6 Hz, CHO), and 5.7 (1 H, q, J 6 Hz, CH=C); δ_C 13.1 (q, CH_3CH), 13.75 (q, CH_3CH_2), 22.1, 27.5, 34.3 (3 t, 3 × CH_2), 75.0 (d, CHO), 120.1 (d, $CH=C$), and 135.0 (s, CCl).

Preparation of the Intermediates (4a) *and* (26) *from the Chlorohydrins* (3a) *and* (3d). *Methods A and C. General Procedure.*—To a stirred solution of the chlorohydrin (3) (15 mmol) in THF (30 ml) was added an ether solution of the corresponding organometallic reagent (ethylmagnesium bromide or phenyl-lithium) (16 mmol) at −15 °C under argon. The reaction mixture was stirred for *ca.* 30 min at the same temperature and then lithium powder (0.32 g, 45 mmol) was added. The resulting mixture was stirred for *ca.* 12 h and the temperature allowed to rise to 20 °C. The suspension was filtered off (G-3) to give the corresponding solution of the intermediate (4a) or (26).

Preparation of the Intermediates (4), (20), (24), *and* (25) *from* (E)-2-*Chlorocrotonaldehyde* (2) *or* 2-*Chloroacrolein* (19). *Method B. General Procedure.*—An ether solution of a Grignard reagent (16 mmol) was added to a stirred solution of the corresponding 2-chloroaldehyde (2) or (19) (15 mmol) in THF (30 ml) at −15 °C under argon. The mixture was stirred for 2 h and the temperature allowed to rise to 20 °C. Then, the corresponding metal [lithium powder, or sodium or potassium plates (see Discussion), 45 mmol] was added to the mixture at −15 °C and it was stirred for *ca.* 12 h and the temperature allowed to rise to 20 °C. The resulting suspension was filtered off (G-3) to give the corresponding solution of the intermediate (4), (20), (24), or (25).

Reaction of the Intermediates (4), (20), *and* (24)—(26) *with Electrophiles. Isolation of Products* (5)—(23). *General Procedure.*—Once the solution of the intermediate (4), (20), or (24)—(26) had been prepared as described above (15 mmol) the corresponding electrophile (15 mmol) was added, the mixture was stirred for 3 h and then hydrolysed with water and neutralized with hydrochloric acid. The resulting solution was extracted with ether, the organic layer was washed with water and dried (Na_2SO_4), the solvents were removed (760 or 15 mmHg) and the residue was distilled under reduced pressure (see Table) to afford the products (5)—(23). (Z)-4-*Deuteriohex-4-en-3-ol* (5) (Found: C, 71.4; H/D, 13.0. $C_6H_{11}DO$ requires C, 71.23; H/D, 12.95%); $v_{max.}$ 3 395 cm^{-1} (OH); δ_H 0.85 (3 H, t, *J* 8 Hz, CH_3CH$_2$), 1.45 (2 H, quintet, *J* 6 Hz, CH$_2$), 1.65 (3 H, d, *J* 6 Hz, CH_3CH), 3.4 (1 H, s, OH), 3.6—3.95 (1 H, m, CHO), and 5.35—5.65 (1 H, m, CH=C); δ_C 9.5 (q, CH$_3$CH$_2$), 17.2 (q, CH$_3$CH), 29.9 (t, CH$_2$), 73.3 (d, CHO), 124.7 (d, CH=C), and 134.3 (t, J_{CD} 23.1 Hz, CD).

(E)-4-*Methylthiohex-4-en-3-ol* (6) (Found: C, 57.5; H, 9.6. $C_7H_{14}OS$ requires C, 57.49; H, 9.65%); $v_{max.}$ 3 400 cm^{-1} (OH); δ_H 0.9 (3 H, t, *J* 8 Hz, CH_3CH$_2$), 1.5—1.75 (2 H, m, CH$_2$), 1.9 (3 H, d, *J* 6 Hz, CH_3CH), 2.2 (3 H, s, CH$_3$S), 2.9—3.5 (1 H, br s, OH), 4.0 (1 H, t, *J* 6 Hz, CHO), and 5.95 (1 H, q, *J* 6 Hz, CH=C); δ_C 9.9 (q, CH$_3$CH$_2$), 14.6 (q, CH$_3$S), 16.7 (q, CH$_3$CH), 28.5 (t, CH$_2$), 76.7 (d, CHO), 128.4 (d, CH=C), and 139.4 (s, C=CH).

Methyl (E)-2-*ethylidene-3-hydroxypentanoate* (7′)† (Found: C, 60.5; H, 8.9. $C_8H_{14}O_3$ requires C, 60.74; H, 8.92%); $v_{max.}$ 3 480 (OH) and 1 725 cm^{-1} (C=O); δ_H 0.9 (3 H, t, *J* 8 Hz, CH_3CH$_2$), 1.55 (2 H, quintet, *J* 6 Hz, CH$_2$), 1.95 (3 H, d, *J* 6 Hz, CH_3CH), 3.1 (1 H, s, OH), 3.7 (3 H, s, CH$_3$O), 3.95—4.2 (1 H, m, CHO), and 6.0—6.35 (1 H, m, CH=C); δ_C 9.5 (q, CH$_3$CH$_2$), 14.7 (q, CH$_3$CH), 29.3 (t, CH$_2$), 50.4 (q, CH$_3$O), 72.7 (d, CHO), 134.5 (d, CH=C), 135.8 (s, C=CH), and 167.4 (s, C=O).

(Z)-3-*Deuteriohept-2-en-4-ol* (8) (Found: C, 72.9; H/D, 13.2. $C_7H_{13}DO$ requires C, 72.99; H/D, 13.12%); $v_{max.}$ 3 360 cm^{-1} (OH); δ_H 0.85 (3 H, t, *J* 8 Hz, CH_3CH$_2$), 1.05—1.45 (4 H, m, 2 × CH$_2$), 1.55 (3 H, d, *J* 6 Hz, CH_3CH), 3.15—3.4 (1 H, br s, OH), 3.7—4.15 (1 H, m, CHO), and 5.25—5.65 (1 H, m, CH=C); δ_C 13.5 (q, CH$_3$CH$_2$), 17.9 (q, CH$_3$CH), 18.3, 39.3 (2 t, 2 × CH$_2$), 71.5 (d, CHO), 124.3 (d, CH=C), and 134.6 (t, J_{CD} 23.2 Hz, CD).

(Z)-*Hepta*-1,5-*dien-4-ol* (9) (Found: C, 75.0; H, 10.7. $C_7H_{12}O$ requires C, 74.95; H, 10.78%); $v_{max.}$ 3 430 cm^{-1} (OH); δ_H 1.7 (3 H, d, *J* 6 Hz, CH$_3$), 2.25 (2 H, t, *J* 6 Hz, CH$_2$C=C), 3.25 (1 H, s, OH), 3.9—4.0 (1 H, m, CHO), 4.75—5.25 (2 H, m, CH$_2$=C), and 5.4—5.95 (3 H, m, 3 × CH=C); δ_C 17.35 (q, CH$_3$), 41.9 (t, CH$_2$C=C), 71.6 (d, CHO), 116.5 (t, CH$_2$=C), 125.3, 134.1, and 134.8 (3 d, 3 × CH=C).

(Z)-5-*Deuteriohepta*-1,5-*dien-4-ol* (10) (Found: C, 74.3; H/D, 11.5. $C_7H_{11}DO$ requires C, 74.29; H/D, 11.58%); $v_{max.}$ 3 440 cm^{-1} (OH); δ_H 1.7 (3 H, d, *J* 6 Hz, CH$_3$), 2.2 (2 H, t, *J* 6 Hz, CH$_2$C=C), 2.3—3.2 (1 H, br signal, OH), 3.95 (1 H, t, *J* 6 Hz, CHO), 4.35—5.35 (2 H, m, CH$_2$=C), and 5.35—6.0 (2 H, m, 2 × CH=C); δ_C 17.3 (q, CH$_3$), 41.9 (t, CH$_2$C=C), 71.5 (d, CHO),

116.5 (t, CH$_2$=C), 133.7 (t, J_{CD} 22.6 Hz, CD), 125.2 and 134.8 (2 d, 2 × CH=C).

(E)-4-*Ethylidene-2-methyloct-7-ene-3,5-diol* (11)† (Found: C, 71.7; H, 11.0. $C_{11}H_{20}O_2$ requires C, 71.69; H, 10.94%); $v_{max.}$ 3 400 cm^{-1} (OH); δ_H 0.75—1.6 (7 H, m, 2 × CH$_3$CH and CHCO), 1.75 (3 H, d, *J* 6 Hz, CH$_3$C=C), 2.2—2.55 (2 H, m, CH$_2$C=C), 4.1 (2 H, s, 2 × OH), 3.95—4.35 (2 H, m, 2 × CHO), 4.8—5.25 (2 H, m, CH$_2$=C), and 5.45—6.0 (2 H, m, 2 × CH=C); δ_C 13.1, 13.3 (2 q, CH$_3$C=C), 18.8, 19.1, 19.4, 19.7 (4 q, 2 × CH$_3$CH), 32.4, 33.1 (2 d, CHCO), 40.0, 42.6 (2 t, CH$_2$C=C), 69.9, 73.4, 75.0, 75.5 (4 d, 2 × CHO), 116.0, 116.4 (2 t, CH$_2$=C), 122.5, 122.9, 135.4, 135.9 (4 d, 2 × CH=C), 141.7, and 142.2 (2 s, C=CH).

(E)-2-*Ethylidene-3-hydroxyhex-4-enal* (12) (Found: C, 68.7; H, 8.6. $C_8H_{12}O_2$ requires C, 68.55; H, 8.63%); $v_{max.}$ 3 460 (OH) and 1 680 cm^{-1} (C=O); δ_H 2.0 (3 H, d, *J* 6 Hz, CH$_3$), 2.15—2.4 (2 H, m, CH$_2$C=C), 3.65 (1 H, s, OH), 4.5 (1 H, t, *J* 6 Hz, CHO), 4.85—5.15 (2 H, m, CH$_2$=C), 5.4—5.65 (1 H, m, CH=CH$_2$), 6.52 (1 H, q, *J* 8 Hz, CHCH$_3$), and 9.25 (1 H, s, CH=O); δ_C 14.9 (q, CH$_3$), 41.0 (t, CH$_2$C=C), 67.1 (d, CHO), 116.9 (t, CH$_2$=C), 134.5, 144.3 (2 d, 2 × CH=C), 151.7 (s, C=CH), and 194.8 (d, CH=O).

(Z)-*Oct-2-en-4-ol* (13) (Found: C, 74.8; H, 12.5. $C_8H_{16}O$ requires C, 74.94; H, 12.58%); $v_{max.}$ 3 380 cm^{-1} (OH); δ_H 0.65—1.0 (3 H, m, CH_3CH$_2$), 1.05—1.45 (6 H, m, 3 × CH$_2$), 1.5—1.7 (3 H, m, CH_3CH), 3.7—3.95 (1 H, m, CHO), 4.2 (1 H, s, OH), and 5.3—5.55 (2 H, m, 2 × CH=C); δ_C 13.8 (q, CH$_3$CH$_2$), 17.3 (q, CH$_3$CH), 22.5, 27.5, 36.9 (3 t, 3 × CH$_2$), 72.1 (d, CHO), 124.8, and 134.9 (2 d, 2 × CH=C).

(Z)-3-*Deuterio-oct-2-en-4-ol* (14) (Found: C, 74.3; H/D, 13.3. $C_8H_{15}DO$ requires C, 74.36; H/D, 13.26%); $v_{max.}$ 3 400 cm^{-1} (OH); δ_H 0.5—0.95 (3 H, m, CH_3CH$_2$), 1.05—1.45 (6 H, m, 3 × CH$_2$), 1.6 (3 H, d, *J* 6 Hz, CH_3CH), 2.1—2.5 (1 H, br s, OH), 3.7—3.95 (1 H, m, CHO), and 5.3—5.65 (1 H, m, CH=C); δ_C 13.8 (q, CH$_3$CH$_2$), 17.2 (q, CH$_3$CH), 22.5, 27.6, 37.0 (3 t, 3 × CH$_2$), 72.0 (d, CHO), 124.5 (d, CH=C), and 134.7 (t, J_{CD} 22.9 Hz, CD).

(E)-3-*Methylthio-oct-2-en-4-ol* (15) (Found: C, 61.9; H, 10.5. $C_9H_{18}OS$ requires C, 62.02; H, 10.41%); $v_{max.}$ 3 420 cm^{-1} (OH); δ_H 0.9—1.05 (3 H, m, CH_3CH$_2$), 1.15—1.75 (6 H, m, 3 × CH$_2$), 1.85 (3 H, d, *J* 6 Hz, CH_3CH), 2.2 (3 H, s, CH$_3$S), 2.25—2.4 (1 H, br s, OH), 3.9—4.1 (1 H, m, CHO), and 5.95 (1 H, q, *J* 6 Hz, CH=C); δ_C 13.7 (q, CH$_3$CH$_2$), 14.5 (q, CH$_3$S), 16.6 (q, CH$_3$CH), 22.4, 27.8, 35.5 (3 t, 3 × CH$_2$), 75.4 (d, CHO), 128.0 (d, CH=C), and 140.0 (s, C=CH).

Methyl (E)-2-*ethylidene-3-hydroxyheptanoate* (16′)† (Found: C, 64.4; H, 9.7. $C_{10}H_{18}O_3$ requires C, 64.49; H, 9.74%); $v_{max.}$ 3 500 (OH) and 1 750 cm^{-1} (C=O); δ_H 0.75—1.0 (3 H, m, CH_3CH$_2$), 1.15—1.6 (6 H, m, 3 × CH$_2$), 1.95 (3 H, d, *J* 6 Hz, CH_3CH), 3.45 (1 H, s, OH), 3.7 (3 H, s, CH$_3$O), 4.1—4.35 (1 H, m, CHO), and 6.0—6.35 (1 H, m, CH=C); δ_C 13.6 (q, CH$_3$CH$_2$), 14.8 (q, CH$_3$CH), 22.3, 27.8, 36.5 (3 t, 3 × CH$_2$), 50.5 (q, CH$_3$O), 71.5 (d, CHO), 134.4 (d, CH=C), 136.4 (s, C=CH), and 167.4 (s, C=O).

(Z)-3-*Deuterio-6-methylhept-2-en-4-ol* (17) (Found: C, 74.4; H/D, 13.2. $C_8H_{15}DO$ requires C, 74.36; H/D, 13.26%); $v_{max.}$ 3 390 cm^{-1} (OH); δ_H 0.8 (6 H, d, *J* 6 Hz, 2 × CH_3CHC), 0.9—1.5 [3 H, m, CH(CH$_3$)$_2$ and CH$_2$], 1.65 (3 H, d, *J* 6 Hz, CH$_3$C=C), 3.25 (1 H, br s, OH), 3.8—4.05 (1 H, m, CHO), and 5.3—5.7 (1 H, m, CH=C); δ_C 17.2 (q, CH$_3$C=C), 22.2, 22.8 (2 q, 2 × CH$_3$CHC), 24.2 [d, CH(CH$_3$)$_2$], 46.5 (t, CH$_2$), 70.1 (d, CHO), 124.3 (d, CH=C), and 135.0 (t, J_{CD} 23.05 Hz, CD).

2-*Deuteriohex-1-en-3-ol* (21) (Found: C, 71.3; H/D 13.0. $C_6H_{11}DO$ requires C, 71.23; H/D, 12.95%); $v_{max.}$ 3 380 cm^{-1} (OH); δ_H 0.7—1.2 (3 H, m, CH$_3$), 1.15—1.7 (4 H, m, CH$_2$CH$_2$), 2.55—2.9 (1 H, br s, OH), 3.8—4.05 (1 H, m, CHO), and 4.85—5.3 (2 H, m, CH$_2$=C); δ_C 13.7 (q, CH$_3$), 18.3, 39.2 (2 t, CH$_2$CH$_2$), 72.0 (d, CHO), 113.1 (t, CH_2=C), and 141.4 (t, J_{CD} 23.4 Hz, CD).

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† See footnotes *c* and *d* in the Table.

2-*Deuteriohexa*-1,5-*dien*-3-*ol* (**22**) (Found: C, 72.7; H/D 11.1. C_6H_9DO requires C, 72.68; H/D, 11.18%); $v_{max.}$ 3 380 cm^{-1} (OH); δ_H 2.25 (2 H, t, *J* 6 Hz, $CH_2C=C$), 3.4—3.6 (1 H, br s, OH), 3.95—4.2 (1 H, m, CHO), 4.9—5.3 (4 H, m, 2 × $CH_2=C$), and 5.55—6.05 (1 H, m, CH=C); δ_C 41.5 (t, $CH_2C=C$), 71.8 (d, CHO), 113.9, 116.9 (2 t, 2 × $CH_2=C$), 134.4 (d, $CH=C$), and 140.3 (t, J_{CD} 23.5, CD).

2-*Methylthiohexa*-1,5-*dien*-3-*ol* (**23**) (Found: C, 58.3; H, 8.4. $C_7H_{12}OS$ requires C, 58.29; H, 8.39%); $v_{max.}$ 3 420 cm^{-1} (OH); δ_H 2.0—2.15 (5 H, m, with s at δ 2.1, $CH_2C=C$ and CH_3S), 3.4—3.6 (1 H, br s, OH), 3.95—4.1 (1 H, m, CHO), 4.8—5.25 (4 H, m, 2 × $CH_2=C$), and 5.5—6.0 (1 H, m, CH=C); δ_C 13.9 (q, CH_3S), 41.0 (t, $CH_2C=C$), 74.2 (d, CHO), 104.1, 116.9 (2 t, 2 × $CH_2=C$), and 150.3 (s, $C=CH_2$).

Thermal Decomposition of the Dianion (**4d**). *General Procedure.*—The intermediate (**4d**) (15 mmol) was obtained as described above. The reaction mixture was filtered off (G-3), the solvents were removed (0.1 mmHg) from the resulting solution and THF or dioxane (25 ml) was added. The solution was refluxed for 2 h and then deuterium oxide (2.0 ml, 100 mmol) was added at room temperature. The mixture was then neutralized with hydrochloric acid, extracted with ether, and the organic layer was washed with water and dried (Na_2SO_4). The solvents were removed (15 mmHg) and the residue was distilled (15 mmHg) to afford the product (**13**) [77% yield based on (**2**)] or (**14**) [71% yield based on (**2**)].

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