Chloromethyl-lithium and 1-Chloro-2-methylprop-1-enyl-lithium: Useful Intermediates in the Synthesis of Unsaturated and Bifunctionalized Compounds[1]

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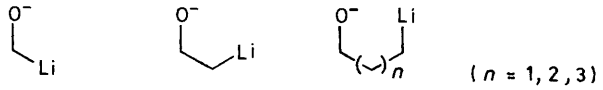
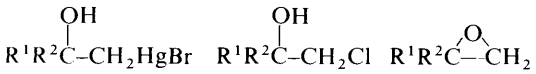
The reaction of *in situ* generated chloromethyl-lithium with ketones (**5**) at −78 °C afforded, after lithiation with lithium naphthalenide at the same temperature, β-oxidoalkyl-lithium compounds (**6**), which on reaction with electrophiles (deuterium oxide, dimethyl disulphide, carbon dioxide, cyclohexanone, and allyl bromide) yielded bifunctionalized compounds (**7**). When the lithiation step was carried out with lithium powder and at temperatures ranging between −60 °C and 20 °C, the corresponding decomposition of intermediates (**6**) derived from aldehydes and ketones (**5**) took place spontaneously giving the corresponding terminal or exocyclic olefins (**11**) regioselectively. The use of *in situ* generated 1-chloro-2-methylprop-1-enyl-lithium as organolithium reagent in the addition to carbonyl compounds (**5**) at −110 °C, followed by transformation of the resulting chlorohydrin (**13**) into the corresponding methyl ether (**14**) (successive treatment with sodium hydride and methyl iodide at 0—20 °C) gave, after lithiation with lithium phenanthrenide at room temperature, the corresponding substituted cumulenes (**12**).

Oxido-functionalized organolithium compounds of the type (**1**), which are sp^3 hybridized d^n (n = 1—5) reagents,[2] are interesting synthons in organic synthesis because they are potential precursors of (*a*) functionalized alcohols by reaction with electrophilic reagents, or (*b*) carbenes, olefins, or carbocycles by an elimination process.



(**1a**) (**1b**) (**1c**)

In relation to the reaction (*a*) with electrophiles, it is important to take into account the stability of intermediates (**1**); thus, whilst γ-,[3] δ-,[4] or ε-oxido[5] organolithium intermediates (**1c**) are stable species, which behave as typical organolithium compounds, the corresponding α-[6] of β-substituted[3b,7] systems [(**1a**) or (**1b**), respectively] are unstable species and have to be prepared at low temperature in order to avoid decomposition processes, mainly elimination reactions. On the other hand, and considering the second possibility (*b*) as a synthetic method, only the β-elimination has been used in the preparation of different types of olefinic systems;[8] in the other cases the elimination either does not take place or yields decomposition products. For these reasons the corresponding β-functionalized derivatives of the type (**1b**) have been the subject of great interest recently, their preparation being carried out at low temperature through three different routes: (*a*) mercury-lithium transmetallation starting from β-substituted organomercury compounds (**2**);[9] (*b*) chlorine-lithium exchange from β-chlorohydrins (**3**);[7] and (*c*) lithium-assisted opening of epoxides (**4**).[10]



(**2**) (**3**) (**4**)

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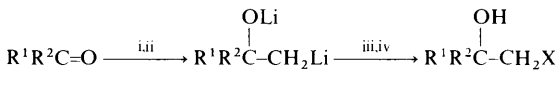
We report here the preparation of intermediates of the type (**1b**) starting from the more available ketones and using *in situ* generated chloromethyl-lithium, their use in organic synthesis by reaction with electrophiles and their capability of yielding olefins by an elimination process. We also report the preparation of cumulenes by using 1-chloro-2-methylprop-1-enyl-lithium and carbonyl compounds.

Results and Discussion

Preparation of β-Oxido Functionalized Organolithium Intermediates (**6**) *and their Reaction with Electrophiles.*—The reaction of different ketones (**5**) with chloromethyl-lithium (generated *in situ* by treatment of chloroiodomethane with methyl-lithium)[11] at −78 °C, followed by lithiation with lithium naphthalenide at the same temperature‡ leads to the corresponding intermediates (**6**). When this dianionic d^2-reagent was treated with different electrophiles such as deuterium oxide, dimethyl disulphide, carbon dioxide, cyclohexanone, or allyl bromide, the expected products (**7**) were obtained, after acid hydrolysis (Scheme 1 and Table 1). When aldehydes (*i.e.*, isopentanal or benzaldehyde) are employed instead of ketones as starting materials, the same process leads to a complicated mixture of reaction products.



(**5**) (**6**) (**7**)

a; $R^1, R^2 = [CH_2]_4$
b; $R^1, R^2 = [CH_2]_5$
c; $R^1, R^2 = [CH_2]_7$
d; $R^1 = R^2$ = Ph
e; R^1 = Me, R^2 = $CHMeCH_2NMe_2$

Scheme 1. *Reagents and conditions:* i, $ClCH_2Li$, −78 °C; ii, $Li^+C_{10}H_8^-$, −78 °C; iii, electrophile = D_2O, Me_2S_2, CO_2, $[CH_2]_5C{=}O$, or $BrCH_2CH{=}CH_2$, −78—20 °C; iv, HCl–H_2O

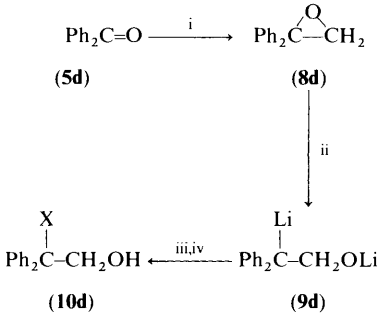
‡ The lithiation with lithium powder at low temperature (−78 °C) failed. Intermediates of the type (**6**) are stable species only below *ca.* −60 °C (see references 7, 9, and 10).

Table 1. Reaction of intermediates (**6**) or (**9d**) with electrophiles to give (**7**) or (**10d**)

Starting ketone	Intermediate	Electrophile	Product (7) or (10d)	X	Yield[a] (%)	B.p. (°C) [mmHg] or m.p. (°C) [solvent]
(**5a**)	(**6a**)	D_2O	(**7aa**)	D	50	55—59 [15]
(**5b**)	(**6b**)	D_2O	(**7ba**)	D	60	37—40 [0.1]
(**5b**)	(**6b**)	Me_2S_2	(**7bb**)	MeS	50	46—50 [0.1]
(**5c**)	(**6c**)	D_2O	(**7ca**)	D	45[b]	43—46 [0.001]
(**5d**)	(**6d**)	D_2O	(**7da**)	D	90	78—80 [CCl_4][c]
(**5d**)	(**6d**)	Me_2S_2	(**7db**)	MeS	95	85—88 [0.001]
(**5d**)	(**6d**)	CO_2	(**7dc**)[d]	CO_2H[d]	91	96—98 [CCl_4][d,e]
(**5d**)	(**6d**)	$[CH_2]_5C{=}O$	(**7dd**)	$[CH_2]_5COH$	90	106—108 [CCl_4]
(**5d**)	(**6d**)	$BrCH_2CH{=}CH_2$	(**7de**)	$CH_2CH{=}CH_2$	74	70—73 [0.001]
(**5e**)	(**6e**)	Me_2S_2	(**7eb**)[f]	MeS	60	45—47 [0.001]
(**5d**)	(**9d**)	Me_2S_2	(**10db**)	MeS	94	77—79 [CCl_4]
(**5d**)	(**9d**)	CO_2	(**10dc**)[d]	CO_2H[d]	72	74—76 [0.001][d]
(**5d**)	(**9d**)	$[CH_2]_5C{=}O$	(**10dd**)	$[CH_2]_5COH$	73	177—179 [CCl_4]

[a] Isolated yield based on the starting ketone (**5**). [b] Lithium 1-dimethylaminonaphthalenide was used instead of lithium naphthalenide. [c] Lit.,[7] b.p. 89—91 °C (0.001 mmHg). [d] Isolated as the methyl ester by treatment of the hydroxy acid with diazomethane. [e] Lit.,[7] m.p. 96—100 °C. [f] A mixture of *erythro*/*threo* isomers (*ca.* 9:1 from g.l.c.) was obtained.

The possibility of obtaining the corresponding regioisomer (**9d**) of intermediate (**6**) was tested starting from benzophenone (**5d**). Thus, when the reaction mixture was allowed to warm to room temperature after the addition of chloromethyl-lithium to (**5d**), the expected cyclization took place yielding the epoxide (**8d**);[11,12] the *in situ* metallation of this compound with lithium naphthalenide at −78 °C[10] yielded the intermediate (**9d**), which on reaction with dimethyl disulphide, carbon dioxide, or cyclohexanone afforded products (**10d**), after acid hydrolysis (Scheme 2 and Table 1). The production of the epoxide (**8d**) in the process (**5d**)→(**10d**) was demonstrated by performing the hydrolysis after the first step of the reaction; compound (**8d**) was isolated in 95% yield.



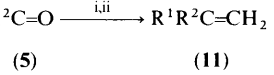
Scheme 2. *Reagents and conditions:* i, $ClCH_2Li$, −78—20 °C; ii, $Li^+ C_{10}H_8^-$, −78 °C; iii, electrophile = Me_2S_2, CO_2, $[CH_2]_5C{=}O$; −78—20 °C; iv, $HCl–H_2O$

Preparation of Terminal and Exocyclic Olefins (**11**) *by* β-*Elimination of Intermediates* (**6**).—The decomposition of intermediates (**6**) by β-elimination was carried out by allowing the reaction mixture to warm to room temperature in the metallation step, which in this case could be performed with lithium powder at temperatures ranging between −60 and 20 °C. Thus, starting from aldehydes or ketones (**5**), the successive addition of chloromethyl-lithium (generated *in situ* as above) at −78 to −60 °C and lithium powder in the above described reaction conditions led to the expected terminal or exocyclic olefins (**11**) (Scheme 3 and Table 2). Obviously the transformation (**5**)→(**11**) involves the intermediate (**6**), which under the reaction conditions undergoes β-elimination[8] to afford the olefins (**11**).

Table 2. Olefins (**11**) from carbonyl compounds (**5**)

Starting carbonyl compound	Olefin (11)	Yield[a] (%)	B.p. (°C) [mmHg]	Lit. b.p. (°C) [mmHg]
(**5b**)	(**11b**)	80	102—104 [760]	102—103 [760][13]
(**5c**)	(**11c**)	80	54—56 [0.1]	154—156 [760][14]
(**5d**)	(**11d**)	60	62—64 [0.1]	165—169 [760][13]
(**5e**)	(**11e**)	50	40—44 [15]	
(**5f**)	(**11f**)	80	44—48 [0.1]	124.5—124.8 [760][15]
(**5g**)	(**11g**)	95	130—134 [760]	130—133 [760][14]
(**5h**)	(**11h**)[b]	43[b]	35—40 [15]	59—60 [20][13]
(**5i**)	(**11i**)	80	144—147 [760]	146 [760][13]
(**5j**)	(**11j**)	55	55—58 [0.1]	156—162 [630][16]

[a] Isolated yield based on the starting carbonyl compound (**5**). [b] Isolated as its 1,2-dibromo derivative.



b; R^1, R^2 = $[CH_2]_5$
c; R^1, R^2 = $[CH_2]_7$
d; R^1 = Me, R^2 = Ph
e; R^1 = Me, R^2 = $CHMeCH_2NMe_2$
f; R^1, R^2 = $[CH_2]_4CHMe$
g; R^1 = Me, R^2 = C_6H_{13}-n
h; R^1 = H, R^2 = Et
i; R^1 = H, R^2 = C_7H_{15}-n
j; R^1 = H, R^2 = PhCHMe

Scheme 3. *Reagents and conditions:* i, $ClCH_2Li$, −78 to −60 °C; ii, Li, −60—20 °C

Preparation of Cumulenes (**12**) *from Carbonyl Compounds and* 1-*Chloro*-2-*methylprop*-1-*enyl-lithium.*—The treatment of

Table 3. Cumulenes (**12**) from carbonyl compounds (**5**)

Starting carbonyl compound	Cumulene (**12**)	Yield[a,b] (%)
(**5b**)	(**12b**)	40
(**5g**)	(**12g**)	40
(**5k**)	(**12k**)	51
(**5l**)	(**12l**)	54
(**5m**)	(**12m**)	51

[a] Isolated yield based on the starting carbonyl compound (**5**). [b] Products (**12**) were isolated by trap-to-trap distillation at reduced pressure (0.1 mmHg, *ca.* 50 °C bath temperature).

different carbonyl compounds (**5**) with 1-chloro-2-methylprop-1-enyl-lithium (generated *in situ* from 1-chloro-2-methylpropene and s-butyl-lithium at −110 °C)[17] at −110 °C led, after hydrolysis with ammonium chloride at the same temperature, to the corresponding chlorohydrin of the type (**13**); this crude product was successively treated with sodium hydride and methyl iodide at temperatures ranging between 0 and 20 °C to afford, after hydrolysis with water, the crude derivative (**14**). The final lithiation of this crude chloro ether (**14**) with lithium phenanthrenide,*[18a] led to an unstable β-lithio ether of the type (**15**), which spontaneously underwent β-elimination[19] to give the cumulene (**12**) (Scheme 4 and Table 3). The transformation of the lithium salt of derivative (**13**) into the chloro ether (**14**) is necessary in order to get a better leaving group to achieve the last β-elimination of (**15**): the corresponding dianion (**16**) would not undergo β-elimination, even in refluxing tetrahydrofuran.[20]

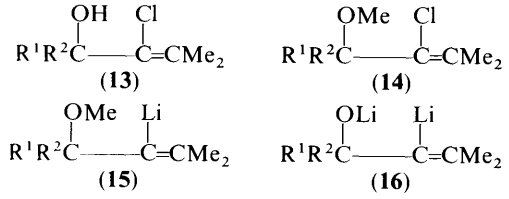
From the chemistry described in this paper, we conclude that it represents a new route for β-oxido functionalized organolithium compounds from available ketones, using chloromethyl-lithium. The β-elimination of these intermediates leads to terminal and exocyclic olefins in a regioselective manner. The use of 1-chloro-2-methylprop-1-enyl-lithium with the same starting materials yields cumulenes *via* the corresponding regioselective β-elimination process.

$$R^1R^2C{=}O \xrightarrow{\text{i–vii}} R^1R^2C{=}C{=}CMe_2$$

(**5**) (**12**)

b: $R^1, R^2 = [CH_2]_5$
g: $R^1 = Me, R^2 = C_6H_{13}$-n
k: $R^1 = R^2 = Et$
l: $R^1 = H, R^2 = Bu$
m: $R^1 = H, R^2 = Bu^i$

Scheme 4. *Reagents and conditions:* i, $Me_2C{=}(Cl)Li$, −110 °C; ii, NH_4Cl H_2O, then extraction; iii, NaH, 0 °C; (iv) MeI, 0—20 °C; v, H_2O, then extraction; vi, $Li^+C_{14}H_{10}^-$, 20 °C; vii, H_2O



(**13**) (**14**) (**15**) (**16**)

* The lithiation with lithium powder under these reaction conditions failed. The use of lithium phenanthrenide instead of lithium naphthalenide facilitates the isolation of products (**12**) in the work-up (see Experimental section).

Experimental

General.—I.r. spectra were determined with a Perkin-Elmer 577 grating spectrophotometer. ^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, unless otherwise stated, and a D_2O capillary was employed as lock reference. The purity of the volatile distilled or condensed products was determined with a g.l.c. Varian Vista 6000 instrument equipped with an OV-101 Chromosorb column. M.s. (e.i.) were recorded with a Hewlett Packard 5987A spectrometer. Elemental analysis was carried out with a Perkin-Elmer 240 Elemental Analyser. Ether refers to diethyl ether. Starting carbonyl compounds (**5**), chloroiodomethane, 1-chloro-2-methylpropene, methyl- or s-butyl-lithium, and the electrophilic reagents were of the best commercial grade available (Aldrich, Fluka, Merck) and were used without further purification. Lithium naphthalenide, lithium 1-dimethylaminonaphthalenide, or lithium phenanthrenide were prepared according to literature methods.[18] Lithium powder (<20 μm Koch-Light) was commercially available. Ether was successively dried with anhydrous calcium chloride, sodium sulphate, sodium, and finally a K–Na (K_3Na) liquid alloy[21] under reflux, and was distilled and stored under argon. Tetrahydrofuran (THF) was successively dried with anhydrous calcium chloride and sodium sulphate; it was then refluxed with potassium, distilled, and stored under argon. All reactions were carried out under argon and all glassware was dried before use. Products (**11b**), (**11d**), (**11h**), and (**11i**) were commercially available (Aldrich) and were characterized by comparison with authentic samples.

Preparation of Intermediates (**6**) *and* (**9d**) *and Reaction with Electrophiles: Isolation of Products* (**7**) *and* (**10d**): *General Procedure.*—To a solution of chloroiodomethane (11 mmol) and the starting ketone (**5**) (10 mmol) in THF (25 ml) was added a 1M ether solution of methyl-lithium (11 mmol) over 15 min at −78 °C under argon and the mixture was stirred for 45 min. The reaction mixture was treated with a solution of lithium naphthalenide (44 mmol) in THF (50 ml) at −78 °C and stirring was continued for 2 h at the same temperature. The corresponding electrophile (40 mmol) or an excess of anhydrous solid carbon dioxide was then added and the mixture was stirred for 1 h at −78 °C, and then allowed to warm to room temperature overnight. The resulting solution was hydrolysed with aqueous hydrochloric acid, extracted with ether, and the ethereal layer dried (Na_2SO_4). The solvents were removed (15 mmHg) and the corresponding products (**7**) isolated after or before sublimation of naphthalene. When lithium 1-dimethylaminonaphthalenide was used [(**5c**)→(**6c**)] or in the case of (**6e**) the products (**7**) were isolated by acidic work-up. In the case of (**9d**) the reaction mixture was allowed to warm to room temperature *in vacuo* (0.1mmHg) before treatment with lithium naphthalenide (22 mmol) as above; the isolation of 1,1-diphenylethylene oxide (**8d**) was carried out by acid hydrolysis after the first addition of chloromethyl-lithium to benzophenone (**5d**). 1-Deuteriomethylcyclopentanol (**7a**); $\nu_{max.}(CCl_4)$ 3 450 cm^{-1} (OH); δ_H 1.0 (2 H, s, CH_2D), 1.0—1.2 (1 H, br, OH), and 1.2—1.7 (8 H, m, 4 × ring CH_2); δ_C 23.6, 40.6 (4 × ring CH_2), 27.2 (t, J_{CD} 19.1 Hz, CH_2D), and 79.4 (COH); *m/z* 101 (M^+, 4%), 85 (17), 72 (100), 71 (17), 67 (15), 59 (29), 58 (13), 57 (20), 44 (37), 43 (16), and 39 (11).

1-Deuteriomethylcyclohexanol (**7ba**); $\nu_{max.}$ 3 360 cm^{-1} (OH); δ_H 1.1 (2 H, s, CH_2D), 1.2—1.7 (10 H, m, 5 × ring-CH_2), and 1.9—2.2 (1 H, br, OH); δ_C 23.4, 26.6, 40.1 (5 × ring CH_2), 29.6 (t, J_{CD} 19.2 Hz, CH_2D), and 69.8 (COH); *m/z* 115 (M^+, 3%), 99 (11), 81 (11), 73 (11), 72 (100), 71 (16), 59 (26), 44 (24), and 43 (11).

1-*Methylthiomethylcyclohexanol* (**7bb**) (Found: C, 59.6; H, 10.0. $C_7H_{16}OS$ requires C, 59.95; H, 10.06%); $\nu_{max.}(CCl_4)$ 3 420

cm^{-1} (OH); δ_H 1.2—1.7 (10 H, m, 5 × ring-CH_2), 1.8—2.1 (1 H, br s, OH), 2.1 (3 H, s, CH_3), and 2.6 (2 H, s, CH_2S); δ_C 17.8 (CH_3), 21.6, 25.5, 36.6 (3 × ring-CH_2), 48.3 (CH_2S), and 71.2 (COH); *m/z* 160 (M^+, 4%), 99 (71), 81 (100), 79 (20), 62 (82), 61 (23), 55 (21), 45 (11), 43 (30), 42 (10), 41 (26), and 39 (22).

1-Deuteriomethylcyclo-octanol (**7ca**); $\nu_{max.}$(CCl_4) 3 390 cm^{-1} (OH); δ_H 1.1 (2 H, s, CH_2D), 1.2—1.7 (14 H, m, 7 × ring-CH_2), and 1.7—2.0 (1 H, br s, OH); δ_C 22.9, 25.2, 28.7, 38.2 (7 × ring-CH_2), 30.0 (t, J_{CD} 19.2 Hz, CH_2D), and 72.9 (COH); *m/z* 143 (M^+, 1%), 82 (11), 72 (100), 67 (13), 59 (34), 44 (27), 41 (13), and 39 (10).

2-Deuterio-1,1-diphenylethanol (**7da**); $\nu_{max.}$(Nujol) 3 400 (OH), 3 030, 3 020, 1 600, and 1 490 cm^{-1} (Ph); δ_H 1.9 (2 H, s, CH_2D), 2.1 (1 H, br s, OH), and 7.0—7.6 (10 H, m, ArH); δ_C 30.1 (t, J_{CD} 19.1 Hz, CH_2D), 76.0 (COH), 126.1, 126.7, 128.0, and 148.4 (ArC); *m/z* 199 (M^+, 5%), 184 (10), 183 (71), 181 (60), 180 (51), 179 (46), 178 (17), 166 (20), 165 (52), 122 (17), 105 (100), 89 (19), 78 (31), 77 (83), 76 (19), 63 (14), 52 (12), 51 (50), 50 (18), 44 (70), and 39 (11).

2-*Methylthio*-1-*diphenylethanol* (**7db**) (Found: C, 73.6; H, 6.7. $C_{15}H_{16}OS$ requires C, 73.73; H, 6.60%); $\nu_{max.}$(film) 3 450 (OH), 3 050, 3 020, 1 600, and 1 490 cm^{-1} (Ph); δ_H 1.9 (3 H, s, CH_3), 3.2 (2 H, s, CH_2), 3.5 (1 H, s, OH), and 7.0—7.6 (10 H, m, ArH); δ_C 16.9 (CH_3), 47.7 (CH_2), 76.7 (COH), 126.2, 126.6, 128.1, and 146.0 (ArC); *m/z* 244 (M^+, 2%), 184 (12), 183 (79), 109 (100), 77 (67), and 51 (13).

Methyl 2-hydroxy-2,2-diphenylpropionate (**7dc**);[7] $\nu_{max.}$ (Nujol) 3 430 (OH), 3 050, 3 030, 1 590, 1 510 (Ph), and 1 710 cm^{-1} (C=O); δ_H 1.3—1.6 (1 H, br s, OH), 3.1 (2 H, s, CH_2), 3.6 (3 H, s, CH_3), and 7.0—7.6 (10 H, m, ArH); δ_C 45.0 (CH_2), 51.4 (CH_3), 76.1 (COH), 125.6, 127.0, 128.1, 146.5 (ArC), and 172.7 (C=O); *m/z* 256 (M^+, 3%), 183 (32), 182 (18), 105 (100), 77 (55), and 51 (18).

1-(2-*Hydroxy*-2,2-*diphenylethyl*)*cyclohexanol* (**7dd**) (Found: C, 80.8; H, 8.3. $C_{20}H_{24}O_2$ requires C, 81.04; H, 8.16%); $\nu_{max.}$(Nujol) 3 520, 3 430 (OH), 3 060, 1 590, and 1 490 (Ph); δ_H 1.0—1.9 (10 H, m, 5 × ring-CH_2), 1.9—2.3 (2 H, m, 2 × OH), 2.5 (2 H, s, CH_2CPh), and 7.0—7.6 (10 H, m, ArH); δ_C 22.1, 25.8, 39.3 (5 × ring-CH_2), 50.8 (CH_2CPh), 74.4, 78.5 (2 × COH), 126.2, 127.0, 128.5, and 149.3 (ArC); *m/z* 278 (M^+ − 18, 4%), 184 (14), 183 (100), 180 (32), 105 (56), and 77 (25).

1,1-*Diphenylpent*-4-*en*-1-*ol* (**7de**) (Found: C, 85.4; H, 7.9. $C_{17}H_{18}O$ requires C, 85.67; H, 7.61%); $\nu_{max.}$(Nujol) 3 420 (OH), 3 050, 3 020, 1 630, 1 600, and 1 490 cm^{-1} (Ph, CH=CH_2); δ_H 2.0—3.0 (5 H, m, CH_2CH_2CO, OH), 4.8—5.2 (2 H, m, CH_2=C), 5.6—6.1 (1 H, m, CH=C), and 7.1—7.9 (5 H, m, ArH); δ_C 28.2, 41.0 (CH_2CH_2CO), 78.1 (COH), 114.7, 126.8, 127.0, 128.5, 139.3, and 148.0 (ArC, CH=CH_2); *m/z* 238 (M^+, 1%), 220 (13), 183 (61), 165 (10), 142 (10), 129 (23), 128 (12), 115 (16), 109 (100), 91 (24), 77 (67), 51 (17), and 39 (10).

erythro,threo-2,3-*Dimethyl*-4-*dimethylamino*-1-*methylthiobutan*-2-*ol* (**7eb**) (Found: C, 56.7; H, 10.9; N, 7.2. $C_9H_{21}NOS$ requires C, 56.50; H, 11.06; N, 7.32%); $\nu_{max.}$(film) 3 200 cm^{-1} (OH); δ_H 0.7 (3 H, d, *J* 6.5 Hz, CH_3CH), 1.0 (3 H, s, CH_3C), 2.1 (3 H, s, CH_3S), 2.2 (6 H, s, 2 × CH_3N), 2.4 (2 H, s, CH_2S), and 2.0—3.0 (4 H, m, $CHCH_2$, OH); δ_C (for the major isomer) 14.9 (CH_3CH), 17.8 (CH_3S), 22.8 (CH_3C), 35.5 (CH), 46.0 (2 × CH_3N), 46.7 (CH_2S), 64.4 (CH_2N), and 77.0 (COH); *m/z* 176 (M^+ − 15, 1%), 130 (10), and 58 (100).

1,1-Diphenyloxirane (**8d**), m.p. 48—51 °C (CCl_4) (lit.,[22] m.p. 52 °C); $\nu_{max.}$(CCl_4) 3 050, 3 030, 1 590, 1 570, and 1 490 cm^{-1} (Ph); δ_H 3.1 (2 H, s, CH_2) and 7.0—7.6 (10 H, m, ArH); δ_C 58.4 (CH_2), 63.6 (CO), 129.5, 129.8, 130.2, and 140.4 (ArC); *m/z* 196 (M^+ 25%), 195 (77), 167 (37), 166 (28), 165 (100), 164 (11), 152 (11), and 105 (13).

2-*Methylthio*-2,2-*diphenylethanol* (**10db**) (Found: C, 73.9; H, 6.6. $C_{15}H_{16}OS$ requires C, 73.73; H, 6.60%); $\nu_{max.}$(Nujol) 3 260 (OH), 3 020, 1 595, and 1 490 cm^{-1} (Ph); δ_H 1.7 (3 H, s, CH_3), 1.8—2.0 (1 H, br s, OH), 4.1 (2 H, s, CH_2), and 7.0—7.6 (10 H, m, ArH); δ_C 12.6 (CH_3), 61.8 (CS), 67.2 (CH_2), 127.6, 129.5, 130.7, and 144.0 (ArC); *m/z* 244 (M^+, 3%), 214 (15), 213 (100), 198 (11), 197 (62), 178 (10), 167 (12), 166 (19), 165 (88), 164 (11), 152 (14), 121 (23), 115 (10), 105 (74), 91 (69), and 67 (29).

Methyl 3-*hydroxy*-2,2-*diphenylpropanoate* (**10dc**) (Found: C, 74.8; H, 6.0. $C_{16}H_{16}O_3$ requires C, 74.98; H, 6.29%); $\nu_{max.}$(Nujol) 3 500 (OH), 3 040, 3 020, 1 595, 1 490 (Ph), and 1 715 cm^{-1} (C=O); δ_H 3.2 (1 H, s, OH), 3.7 (3 H, s, CH_3), 4.1 (2 H, s, CH_2), and 7.1—7.4 (10 H, m, ArH); δ_C 52.0 (CH_3), 62.1 (*C*Ph), 67.8 (CH_2), 127.5, 128.7, 129.5, 141.8 (ArC), and 174.9 (C=O); *m/z* 227 (M^+ − 29, 15%), 226 (95), 197 (25), 195 (12), 194 (75), 167 (24), 166 (70), 165 (100), 164 (11), 152 (12), 105 (41), 91 (18), and 77 (20).

1-(2-*Hydroxy*-1,1-*diphenylethyl*)*cyclohexanol* (**10dd**) (Found: C, 81.0; H, 8.4. $C_{20}H_{24}O_2$ requires C, 81.04; H, 8.16%); $\nu_{max.}$(Nujol) 3 530, 3 450 (OH), 3 030, 3 020, 1 590, and 1 490 cm^{-1} (Ph); δ_H($CDCl_3$) 1.0—2.5 (11 H, m, 5 × ring-CH_2, OH), 3.6 (1 H, s, OH), 4.6 (2 H, s, CH_2O), and 7.1—7.7 (10 H, m, ArH); δ_C($CDCl_3$) 20.8, 23.1, 33.0 (5 × ring-CH_2), 59.0 (*C*Ph), 68.7 (CH_2O), 74.8 (CO), 125.9, 126.6, 130.6, and 143.7 (ArC); *m/z* 296 (M^+, 1%), 181 (15), 180 (100), 179 (21), 178 (11), 165 (39), 105 (10), and 91 (11).

Preparation of Olefins (**11**): *General Procedure*.—To a solution of chloroiodomethane (11 mmol) and the starting carbonyl compound (**5**) (10 mmol) in THF (25 ml) was added a 1M ether solution of methyl-lithium (11 mmol) over 15 min at −78 °C under argon. The mixture was stirred for 45 min, the temperature being allowed to rise to −60 °C. Lithium powder (45 mmol) was then added and the resulting suspension was stirred for 6 h at the same temperature then overnight, the mixture being allowed to warm to room temperature. The mixture was hydrolysed with aqueous hydrochloric acid, extracted with ether and the ethereal layer dried (Na_2SO_4) and evaporated (15 mmHg). The resulting residue was distilled to afford the olefin (**11**). Product (**11h**) was isolated as its 1,2-dibromo derivative following the literature method.[23] Methylenecyclo-octane (**11c**);[14] $\nu_{max.}$(CCl_4) 3 065 and 1 645 cm^{-1} (CH_2=C); δ_H 1.8—2.3, 2.5—2.8 (10 and 4 H, 2m, 7 × ring-CH_2), and 4.7 (2 H, s, CH_2=C); δ_C 26.5, 27.4, 28.2, 35.8 (7 × ring-CH_2), 111.6 (CH_2=C), and 151.9 (*C*=CH_2); *m/z* 124 (M^+, 3%), 96 (57), 95 (20), 82 (25), 81 (100), 79 (17), 69 (16), 68 (26), 67 (56), 55 (20), 54 (14), 53 (20), 41 (28), 39 (34), and 27 (10).

2,3-*Dimethyl*-4-*dimethylaminobut*-1-*ene* (**11e**) (Found: C, 75.8; H, 13.5; N, 10.8. $C_8H_{17}N$ requires C, 75.52; H, 13.47; N, 11.01%); $\nu_{max.}$(film) 3 070 and 1 645 cm^{-1} (CH_2=C); δ_H 0.9 (3 H, d, *J* 7 Hz, CH_3CH), 1.6 (3 H, s, CH_3C), 1.9—2.3 (3 H, m, $CHCH_2$), 2.1 (6 H, s, 2 × CH_3N), and 4.6 (2 H, s, CH_2=C); δ_C 18.1, 19.7 (2 × CH_3C), 39.2 (CH), 45.9 (2 × CH_3N), 65.3 (CH_2), 110.0 (CH_2=C), and 149.0 (*C*=CH_2); *m/z* 127 (M^+, 1%) and 58 (100).

2-Methylmethylenecyclohexane (**11f**);[15] $\nu_{max.}$(film) 3 080 and 1 640 cm^{-1} (CH_2=C); δ_H 1.0 (3 H, d, *J* 6 Hz, CH_3), 1.3—2.3 (9 H, m, 4 × ring-CH_2, CH), and 4.4—4.6 (2 H, m, CH_2=C); δ_C 18.7 (CH_3), 26.4, 29.1, 36.5, 37.2, 38.0 (4 × ring-CH_2, CH), 104.7 (CH_2=C), and 153.5 (*C*=CH_2); *m/z* 110 (M^+, 48%), 95 (82), 82 (36), 81 (60), 79 (16), 77 (11), 69 (10), 68 (42), 67 (100), 65 (10), 55 (20), 54 (19), 53 (39), 51 (12), 41 (52), 40 (13), and 39 (72).

2-Methyloct-1-ene (**11g**);[14] $\nu_{max.}$(film) 3 070 and 1 645 cm^{-1} (CH_2=C); δ_H 0.8 (3 H, t, *J* 6 Hz, CH_3CH_2), 1.1—1.5 (8 H, m, $CH_3[CH_2]_4$), 1.6 (3 H, s, CH_3C), 1.8—2.1 (2 H, m, CH_2C=C), and 4.5 (2 H, s, CH_2=C); δ_C 14.1 (CH_3CH_2), 22.2, 23.0, 28.0, 29.4, 37.2, 32.2 (5 × CH_2, CH_3C), 109.9 (CH_2=C), and 145.3 (*C*=CH_2); *m/z* 126 (M^+, 6%), 70 (11), 69 (26), 57 (22), 56 (100), 55 (36), 43 (21), 42 (13), 41 (58), and 39 (43).

3-Phenylbut-1-ene (**11j**);[16] $\nu_{max.}$(film) 3 060, 3 030, 1 645, 1 600, and 1 490 cm^{-1} (Ph, CH_2=CH); δ_H 1.3 (3 H, d, *J* 6 Hz,

CH_3), 3.3–3.5 (1 H, m, C*H*Ph), 4.8—5.1 (2 H, m, CH_2=C), 5.7—6.1 (1 H, m, C*H*=CH_2), and 6.9—7.3 (5 H, m, ArH); δ_C 21.4 (CH_3), 43.8 (*C*HPh), 113.7 (*C*H_2=C), 126.7, 127.8, 128.8, 128.9 (ArC), and 143.7 (*C*H=CH_2); *m/z* 132 (M^+, 23%), 131 (12), 117 (100), 115 (41), 91 (90), and 77 (12).

Preparation of Cumulenes (**12**): *General Procedure.*—A solution of 1-chloro-2-methylpropene in THF (5 ml) was added dropwise to a solution of s-butyl-lithium (15 mmol, in hexane *ca.* 1.4M) in ether (10 ml), THF (40 ml), and hexane (10 ml) at −110 °C under argon and the mixture was stirred for 45 min at the same temperature. To the resulting mixture was added the corresponding carbonyl compound (**5**) (10 mmol) in THF (5 ml), and stirring was continued for 4 h at −110 °C. The mixture was then hydrolysed with a saturated aqueous solution of ammonium chloride, extracted with ether and the organic layer dried (Na_2SO_4) and evaporated (15 mmHg). The residue [*ca.* 6 mmol of compound (**13**) from n.m.r. and g.l.c.] was dissolved in THF (10 ml) and sodium hydride (12 mmol) was added to the resulting solution at 0 °C. After being stirred for 15 min at the same temperature, methyl iodide (12 mmol) was added and the mixture was stirred overnight the temperature being allowed to rise to 20 °C. It was then hydrolysed with water, extracted with ether and the organic layer dried (Na_2SO_4) and evaporated (15 mmHg). The residue [*ca.* 5 mmol of compound (**14**) from n.m.r. and g.l.c.] was dissolved in THF (5 ml) and to the resulting solution was added a 0.5M THF solution of lithium phenanthrenide (10 mmol); the mixture was then stirred overnight. It was then hydrolysed with water, extracted with ether, and the organic layer dried (Na_2SO_4): the solvents were then carefully distilled at normal pressure. The resulting residue was condensed trap-to-trap *in vacuo* (0.1 mmHg, *ca.* 50 °C bath temperature) to afford products (**12**). *1-Cyclohexylidene-2-methylpropene* (**12b**) (Found: C, 86.5; H, 13.1. $C_{10}H_{18}$ requires C, 86.88; H, 13.12%); $\nu_{max.}$(film) 1 970 cm^{-1} (C=C=C); δ_H 1.4—1.5 (6 H, m, [CH_2]$_3$$CH_2$C=C), 1.55 (6 H, s, 2 × CH_3), and 1.9—2.0 (4 H, m, 2 × CH_2C=C); δ_C 21.8 (2 × CH_3), 26.2, 28.5, 32.2 (5 × ring CH_2), 92.4, 100.1 (*C*=C=*C*), and 197.6 (C=*C*=C); *m/z* 138 (M^+, 1%), 136 (100), 121 (48), 107 (36), 93 (98), 92 (12), 91 (30), 80 (16), 79 (48), 77 (24), 67 (20), and 55 (10).

2,4-Dimethyldeca-2,3-diene (**12g**) (Found: C, 86.3; H, 13.6. $C_{12}H_{22}$ requires C, 86.67; H, 13.33%); $\nu_{max.}$(CCl_4) 1 950 cm^{-1} (C=C=C); δ_H($CDCl_3$) 0.8—1.0 (3 H, m, CH_3CH_2), 1.2—1.4 (8 H, m, CH_3[CH_2]$_4$), 1.65 (3 H, s, CH_3CCH_2), 1.7 (6 H, s, CH_3CCH_3), and 1.8—2.0 (2 H, m, CH_2C=C); δ_C 14.0 (CH_3CH_2), 21.7 (CH_3CCH_3), 19.6, 23.0, 27.8, 29.1, 32.6, 35.1 (5 × CH_2, CH_3CCH_2), 93.2, 96.8 (*C*=C=*C*), and 200.0 (C=*C*=C); *m/z* 166 (M^+, 2%), 109 (10), 96 (100), 95 (10), 81 (54), 79 (10), and 67 (13).

4-Ethyl-2-methylhexa-2,3-diene (**12k**) (Found: C, 86.6; H, 13.2. C_9H_{16} requires C, 87.02; H, 12.98%); $\nu_{max.}$(CCl_4) 1 960 (very weak) cm^{-1} (C=C=C); δ_H($CDCl_3$) 0.9 (6 H, t, *J* 7 Hz, 2 × CH_3CH_2), 1.6 (6 H, s, CH_3CCH_3), and 1.8 (4 H, q, *J* 7 Hz, 2 × CH_2); δ_C($CDCl_3$) 12.4 (2 × CH_3CH_2), 21.1 (CH_3CCH_3), 25.9 (2 × CH_2), 96.1, 105.4 (*C*=C=*C*), and 198.0 (C=*C*=C); *m/z* 124 (M^+, 100), 109 (48), 95 (83), 93 (19), 91 (11), 81 (21), 79 (19), 77 (17), 67 (85), 55 (27), 53 (13), and 41 (13).

2-Methylocta-2,3-diene (**12l**) (Found: C, 86.7: H, 13.1. C_9H_{16} requires C, 87.02; H, 12.98%); $\nu_{max.}$(CCl_4) 1 960 cm^{-1} (C=C=C); δ_H($CDCl_3$) 0.8 (3 H, t, *J* 7 Hz, CH_3CH_2), 1.2—1.4 (4 H, m, $CH_3CH_2CH_2$), 1.6 (6 H, s, 2 × CH_3C=C), 1.8—2.0 (2 H, m, CH_2C=C), and 4.84 (1 H, m, CH); δ_C(CCl_4) 13.6 (CH_3CH_2), 20.4 (2 × CH_3C=C), 21.5, 28.3, 31.2 (3 × CH_2), 86.8, 93.1 (*C*=C=*C*), and 204.3 (C=*C*=C); *m/z* 124 (M^+, 29%), 109 (58), 82 (54), 81 (38), 79 (37), 77 (12), 67 (100), 65 (12), 55 (11), 53 (16), 41 (24), and 39 (19).

2,6-Dimethylhepta-2,3-diene (**12m**) (Found: C, 87.0; H, 12.7. C_9H_{16} requires C, 87.02; H, 12.98%); $\nu_{max.}$(CCl_4) 1 960 cm^{-1} (C=C=C); δ_H 0.85 (6 H, d, *J* 7 Hz, 2 × CH_3CH), 1.6, 1.65 (6 H, 2 s, 2 × CH_3C=C), 1.8—2.0 (3 H, m, $CHCH_2$), and 4.7—4.9 (1 H, m, CH=C); δ_C 19.9 (2 × CH_3CH), 21.6 (2 × CH_3C=C), 28.4, 38.6 (CH_2CH), 86.3, 94.2 (*C*=C=C), and 205.5 (C=*C*=C); *m/z* 124 (M^+, 24%), 109 (49), 82 (60), 81 (36), 79 (37), 77 (11), 69 (10), 68 (11), 67 (100), 65 (11), 55 (17), 53 (19), 43 (12), 41 (28), and 39 (18).

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