Synthesis of Mono and *gem*-Dihalogeno-olefins from Carbonyl Compounds and *in situ* Generated Lithium Carbenoids

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The treatment of carbonyl compounds (**5**) with dihalogenomethane and lithium dicyclohexylamide at $-78\,^{\circ}\mathrm{C}$ leads after acid hydrolysis to the crude alcohols (**6**), which by silylation with trimethylchlorosilane–hexamethyldisilazane–pyridine affords the crude silylated alcohols (**7**); final treatment of compound (**7**) with lithium di-isopropylamide or butyl-lithium (when one of the halogens is bromine) at low temperature gives the corresponding di- or mono-halogenated olefins (**8**) or (**9**), respectively, through a sole β-elimination process.

Recently we have reported the utility of using lithium carbenoids such as *in situ* generated chloromethyl-lithium[1] for the preparation of terminal and exocyclic olefins,[2] cyclopropanols,[3] β-oxido functionalized organolithium intermediates, bifunctionalized organic compounds,[4] and allyl alcohols[5] by reaction with carbonyl compounds. These results prompted us to study the possibility of working with halogenated lithium carbenoids in order to obtain halogenated olefins, by a β-elimination reaction[2,6] from the corresponding β-functionalized organolithium intermediates.[4] A similar process was described some time ago in the literature,[7,8] starting from chlorinated silyl ethers of the type (**1**); the deprotonation (X = H) or chlorine–lithium exchange (X = Cl) from compounds (**1**) leads to the expected intermediates (**2**), which can undergo α- or β-elimination to yield a mixture of α-chlorinated carbonyl compounds (**3**) or dichloro-olefins (**4**) respectively. In the last case, the use of an excess of the metallation agent leads for $R^1 = H$ to the corresponding terminal alkynes or chloroalkynes. The process can sometimes be directed to a major product depending on steric factors: for R^1, R^2 = bulky alkyl the α-elimination is preferred and for $R^1 = H$ the β-elimination is the most important process (Scheme 1).

In the present paper we have used a methodology of this type for the regioselective preparation of mono- or di-halogenated olefins with both halogen atoms (Hal = Cl, Br) equal or different from a sole β-elimination process.

Results and Discussion

The reaction of different aldehydes or ketones (**5**) with a mixture of dihalogenomethane and lithium dicyclohexylamide[9] at $-78\,^{\circ}\mathrm{C}$ leads after acid hydrolysis to the crude alcohols (**6**); the products were silylated *in situ* with trimethylchlorosilane and hexamethyldisilazane (HMDS)–pyridine[10] to afford the crude silylated alcohols (**7**); these were transformed at low temperature into the corresponding olefins (**8**) by deprotonation with lithium di-isopropylamide or (**9**) by lithium–bromine exchange with butyl-lithium (Scheme 2 and Table 1).

Obviously, formation of the final unsaturated compound takes place through a β-elimination process,[2,6] which involves a β-functionalized organolithium compound[4] of the type (**10**) (Scheme 3).

The participation of compounds (**6**) and (**7**) in the process (**5**) ⟶ (**8**) or (**9**) was shown from the n.m.r. spectra of the crude systems. In Table 2 are listed the ^{13}C n.m.r. data for compounds (**6**) and (**7**).

When $R^1 \neq R^2$ in the starting carbonyl, the corresponding
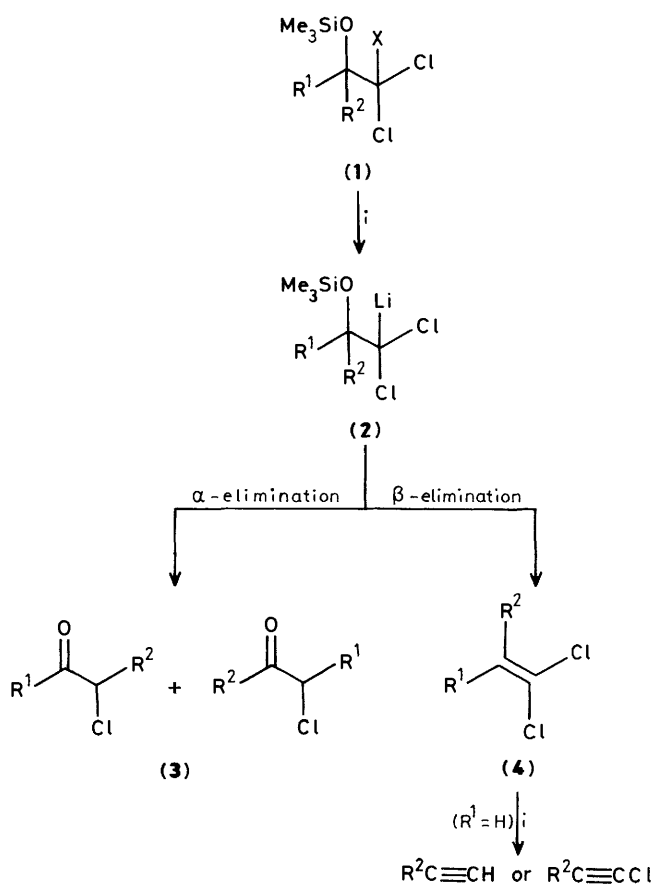
**Scheme 1.** *Reagents:* i, BuLi (X = H, Cl) or $[CH_2]_5NLi$ (X = H)

mixture of olefins was obtained; these products (**9a—d**) were isolated as a *ca.* 1:1 mixture of both Z/E-isomers (by g.l.c.) (see Table 1, entries 1—4 and footnote *b*).

The differences between our results and those previously reported[7,8] are: (*a*) only the β-elimination process is observed;[7,8] (*b*) the method is general and allows the preparation of mono- or di-halogenated olefins with equal or different halogen atoms; and (*c*) the *in situ* generation of starting material of the type (**1**) from carbonyl compounds; so, the whole process represents a transformation of aldehydes and ketones into halogenated olefins.

Table 1. Transformation of carbonyl compounds (**5**) into halogenated olefins (**8**) or (**9**) through intermediates (**6**) and (**7**)

	Starting carbonyl compound (5)		Dihalogeno-methane		Alcohol (6)		Silyl ether (7)		Products (8) or (9)		
Entry	R^1	R^2	X^1	X^2	No.	Yield (%)[a]	No.	Yield (%)[a]	No.	Yield (%)[b]	B.p. (°C) (mmHg)
1	H	$n\text{-}C_7H_{15}$	Br	Cl	(6a)	70	(7a)	63	(9a)[c]	75 (1:1)	84—87 (15)
2	H	$n\text{-}C_7H_{15}$	Br	Br	(6b)	65	(7b)	58	(9b)[c]	65 (1.3:1)	96—99 (15)
3	Me	Ph	Br	Cl	(6c)	76	(7c)	60	(9c)[c]	71 (1.5:1)	44—47 (0.1)
4	Me	Ph	Br	Br	(6d)	65	(7d)	50	(9d)[c]	58 (1.1:1)	35—40 (0.0001)
5	Et	Et	Br	Cl	(6e)	65	(7e)	58	(9e)	82	31—35 (15)[d]
6	Et	Et	Br	Br	(6f)[e]	70	(7f)	59	(8f)	60	82—85 (15)
7									(9f)	66	37—40 (15)
8	[CH₂]₅		Br	Cl	(6g)	90	(7g)	81	(8g)	80	93—97 (15)
9									(9g)	77	51—54 (15)[f]
10	[CH₂]₅		Br	Br	(6h)[g]	91	(7h)	77	(8h)	70	103—106 (15)[h]
11									(9h)	80	58—61 (15)[i]
12	[CH₂]₃		Cl	Cl	(6i)[g]	99	(7i)	95	(8i)	90	81—84 (15)[j]

[a] Isolated crude yield based on the starting carbonyl compound (**5**); the product was pure enough for the next step (purity controlled by n.m.r.; see Table 2). [b] Isolated yield after purification based on the crude compound (**7**); the ratio of isomers (by g.l.c.) is given in parenthesis. [c] Mixture of *Z/E*-isomers. [d] Lit.,[11] no b.p. reported. [e] Lit.,[12] [f] Lit.,[13] b.p. 55 °C(17 mmHg). [g] Lit.,[9] [h] Lit.,[14] b.p. 57—59 °C (0.38 mmHg). [i] Lit.,[15] b.p. 75—79 °C (5 mmHg). [j] Lit.,[7] b.p. 80 °C (13 mmHg).
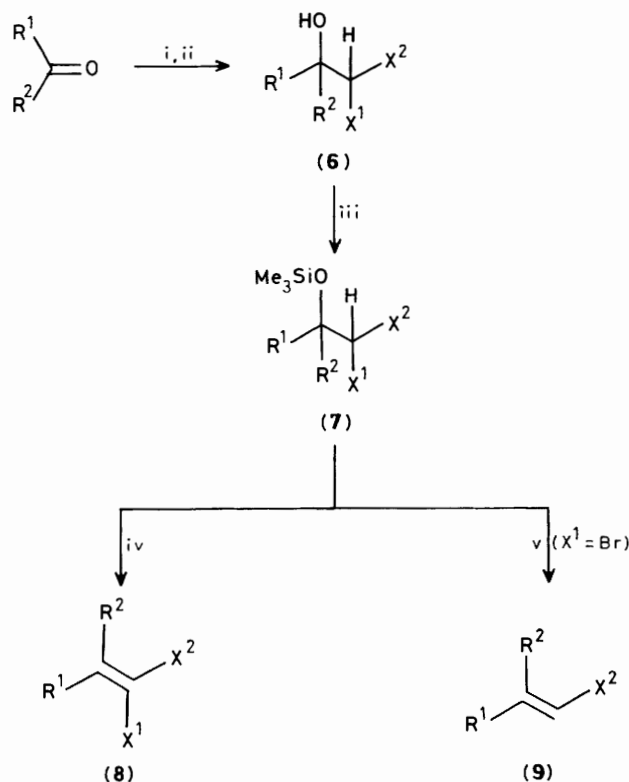
Scheme 2. *Reagents and conditions:* i, $CH_2X^1X^2$, Cy_2NLi, −78 °C; ii, HCl–H₂O, then extraction; iii, Me₃SiCl, (Me₃Si)₂NH, Py, then extraction; iv, Pr^i_2NLi, −50 to −30 °C; v, BuLi, −78 to −60 °C
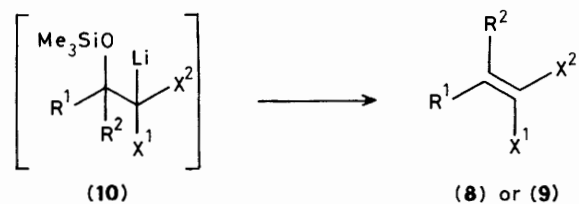
Scheme 3.

Table 2. ¹³C N.m.r. data [δ values; 20 MHz (CCl₄)] for compounds (**6**) and (**7**)

Compound

(**6a**)   14.2 (CH₃), 22.8, 26.0, 29.4, 29.6, 32.0. 32.2 (6 × CH₂), 66.8 (CHBrCl), and 76.0 (CHO)

(**6b**)   14.5 (CH₃), 22.8, 26.5, 30.0, 30.5, 32.5, 33.5 (6 × CH₂), 54.0 (CHBr₂), and 77.2 (CHO)

(**6c**)[c]   26.5, 26.7 (CH₃), 71.0, 71.4 (CHBrCl), 78.0 (CO), 126.7, 128.4, 128.9, 129.2, 129.5, 134.0, 143.2, and 143.5 (ArC)

(**6d**)   27.0 (CH₃), 59.6 (CHBr₂), 77.8 (CO), 127.2, 129.2, 129.4, and 144.0 (ArC)

(**6e**)   8.0 (2 × CH₃), 28.5 (2 × CH₂), 71.8 (CHBrCl), and 78.5 (CO)

(**6f**)   8.8 (2 × CH₃), 29.2 (2 × CH₂), 60.0 (CHBr₂), and 78.2 (CO)

(**6g**)   23.0 (2 × CH_2CH_2CO), 26.5 [$CH_2(CH_2)_2CO$], 33.0, 34.0 (2 × CH_2CO), 73.7 (CHBrCl), and 76.2 (CO).

(**6h**)   22.9 (2 × CH_2CH_2CO), 26.3 [$CH_2(CH_2)_2CO$], 34.0 (2 × CH_2CO), 61.8 (CHBr₂), and 75.5 (CO)

(**6i**)   22.5 (2 × CH_2CH_2CO), 26.0 [$CH_2(CH_2)_2CO$], 33.0 (2 × CH_2CO), 75.5 (CO), and 82.5 (CHCl₂)

(**7a**)   1.5 (3 × CH₃Si), 14.2 (CH_3CH_2), 23.0, 25.5, 29.5, 29.8, 32.0, 33.8 (6 × CH₂), 65.3 (CHBrCl), and 78.2 (CHO)

(**7b**)   1.5 (3 × CH₃Si), 14.5 (CH_3CH_2), 23.5, 26.5, 30.0, 30.5, 33.0, 34.8 (6 × CH₂), 53.8 (CHBr₂), and 78.5 (CHO)

(**7c**)[a]   3.0 (3 × CH₃Si), 23.8, 24.2 (CH_3CO), 71.5, 72.0 (CHBrCl), 81.0, 81.2 (CO), 128.0, 128.1, 129.9, 130.0, 130.1, 145.0, and 145.1 (ArC)

(**7d**)   3.0 (3 × CH₃Si), 24.8 (CH_3CO), 59.6 (CHBr₂), 80.5 (CO), 127.9, 129.0, and 144.5 (ArC)

(**7e**)   3.0 (3 × CH₃Si), 8.2, 8.6 (2 × CH_3CH_2), 29.2, 29.5 (2 × CH₂), 70.0 (CHBrCl), and 82.2 (CO)

(**7f**)   3.0 (3 × CH₃Si), 8.5 (2 × CH_3CH_2), 29.5 (2 × CH₂), 57.8 (CHBr₂), and 81.3 (CO)

(**7g**)   3.1 (3 × CH₃Si), 22.9 (2 × CH_2CH_2CO), 26.1 [$CH_2(CH_2)_2CO$], 34.6, 35.5 (2 × CH_2CO), 71.8 (CHBrCl), and 80.0 (CO)

(**7h**)   2.9 (3 × CH₃Si), 22.5 (2 × CH_2CH_2CO), 25.5 [$CH_2(CH_2)_2CO$], 35.0 (2 × CH_2CO), 59.0 (CHBr₂), and 75.5 (CO).

(**7i**)   3.2 (3 × CH₃Si), 22.9 (2 × CH_2CH_2CO), 26.0 [$CH_2(CH_2)_2CO$], 35.0 (2 × CH_2CO), 80.1 (CO), and 81.8 (CHCl₂)

[a] Mixture of diastereoisomers.

Experimental

General.—For general information see ref. 6.

Preparation of Di- or Mono-halogenated Olefins (8) *and* (9). *General Procedure.*—To a stirred solution of the corresponding carbonyl compound (5) (10 mmol) and dihalogenomethane (20 mmol) in THF (20 ml) was added a THF solution of lithium dicyclohexylamide [20 mmol; from dicyclohexylamine (20 mmol) and butyl-lithium (1.6M in hexane; 20 mmol) in THF (20 ml)] at −78 °C under argon. After being stirred for 2 h at the same temperature, the mixture was hydrolysed with 5M hydrochloric acid, and extracted with ether. The organic layer was dried (Na_2SO_4) and concentrated and the resulting residue, containing the crude compound (6) (^{13}C n.m.r.; see Table 2), was dissolved in pyridine (30 ml). This solution was then treated with HMDS (6 mmol) and trimethylchlorosilane (12 mmol) for R^1 = H (18 and 36 mmol, respectively for $R^1 \neq$ H) at 0 °C. After being stirred for 2 h at room temperature for R^1 = H (16 h at 50 °C for $R^1 \neq$ H) the resulting mixture was hydrolysed with saturated aqueous NH_4Cl, extracted with ether, and the organic layer dried (Na_2SO_4) and concentrated. A portion of the residue, containing the crude compound (7) (^{13}C n.m.r.; see Table 2) (5 mmol) was dissolved in THF (20 ml) and treated with butyl-lithium (1.6M hexane solution; 5.5 mmol; −78 °C) or lithium di-isopropylamide [prepared from di-isopropylamine (6 mmol) in THF (6 ml) and butyl-lithium (1.6M hexane solution; 6 mmol); −60 °C] at low temperature under argon. Stirring was continued, the temperature being allowed to rise to −60 °C over 1 h in the first case, or the mixture was stirred at −60 °C for 4 h in the second. The resulting mixture was hydrolysed with saturated aqueous NH_4Cl and extracted with ether. The organic layer was dried (Na_2SO_4) and concentrated and the resulting residue was distilled at reduced pressure to afford the corresponding halogenated olefin (9) or (8). (Z/E)-1-*Chloronon*-1-*ene* (9a) (Found: C, 67.0; H, 10.4. $C_9H_{17}Cl$ requires C, 67.27; H, 10.66%); $v_{max.}$(film) 3 060 and 1 620 cm⁻¹ (CH=C); δ_H(CDCl₃) 0.9 (3 H, t, *J* 6 Hz, CH₃), 1.2—1.4 [10 H, m, (CH₂)₅CH₃], 2.0—2.3 (2 H, m, CH₂C=C), and 5.6—6.1 (2 H, m, CH=CH); δ_C(CCl₄) 14.3 (CH₃), 23.0, 27.1, 28.5, 29.5, 29.6, 31.0, 32.1 (6 × CH₂), 117.7, 118.9 (CHCl), 132.3, and 134.3 (CH=CCl); *m/z* 162 (*M⁺* + 2, 52%), 160 (*M⁺*, 16), 104 (15), 95 (23), 83 (24), 82 (33), 81 (19), 77 (12), 75 (29), 70 (61), 69 (54), 68 (20), 67 (27), 57 (31), 56 (80), 55 (47), 54 (13), 53 (23), 43 (100), 42 (19), 41 (60), and 39 (37).

(Z/E)-1-*Bromonon*-1-*ene* (9b) (Found: C, 52.4; H, 8.1. $C_9H_{17}Br$ requires C, 52.70; H, 8.35%); $v_{max.}$(CCl₄) 3 060 and 1 614 cm⁻¹ (CH=C); δ_H(CDCl₃) 0.9 (3 H, t, *J* 6 Hz, CH₃), 1.3—1.5 [10 H, m, (CH₂)₅CH₃], 2.0—2.3 (2 H, m, CH₂C=C), and 6.0—6.2 (2 H, m, CH=CH); δ_C(CCl₄) 14.0 (CH₃), 23.0, 28.5, 29.0, 29.3, 29.5, 30.0, 32.2, 33.6 (6 × CH₂), 105.0, 108.5 (CHBr), 136.0, and 139.2 (CH=CBr); *m/z* 206 (*M⁺* + 2, 8%), 204 (*M⁺*, 8), 121 (20), 119 (20), 95 (12), 83 (54), 82 (11), 81 (12), 70 (36), 69 (100), 67 (27), 57 (26), 56 (44), 55 (56), 53 (26), 43 (77), 42 (12), 41 (66), and 39 (47).

(Z/E)-1-*Chloro*-2-*phenylpropene* (9c) (Found: C, 70.5; H, 5.7. C_9H_9Cl requires C, 70.83; H, 5.9%); $v_{max.}$(film) 3 075, 3 060, 3 010, 1 610, 1 590, and 1 480 cm⁻¹ (CH=C); δ_H(CCl₄) 2.0, 2.1 (3 H, 2 d, *J* 1.5 Hz, CH₃), 6.05, 6.25 (1 H, 2 d, *J* 1.5 Hz, CHCl), and 7.2—7.3 (5 H, m, ArH); δ_C(CCl₄) 16.6, 23.0 (CH₃), 113.0, 116.1, 126.3, 128.0, 128.4, 128.7, 129.4, 132.0, and 138.8 (ArC, C=CCl); *m/z* (*M⁺* + 2, 33%), 152 (*M⁺*, 100), 117 (44), 116 (15), 115 (78), 103 (36), 102 (15), 91 (20), 89 (10), 78 (41), 77 (11), 63 (12), and 51 (15).

(Z/E)-1-*Bromo*-2-*phenylpropene* (9d) (Found: C, 54.6; H, 4.3. C_9H_9Br requires C, 54.85; H, 4.60%); $v_{max.}$(film) 3 080, 3 060, 3 020, 1 610, 1 600, and 1 490 cm⁻¹ (CH=C); δ_H(CDCl₃) 2.3, 2.5 (3 H, 2 d, *J* 1.5 Hz, CH₃), 6.5, 6.75 (1 H, 2 d, *J* 1.5 Hz, CHBr), and 7.6—7.7 (5 H, m, ArC); δ_C(CCl₄) 19.8, 25.0 (CH₃), 102.1, 105.9,

127.2, 129.0, 129.5, 130.0, 133.2, and 142.0 (ArC, C=CCl); *m/z* 198 (*M⁺* + 2, 57%), 196 (*M⁺*, 59), 117 (60), 116 (23), 115 (100), 102 (20), 91 (40), 78 (21), 63 (11), 57 (11), and 51 (12).

1-*Chloro*-2-*ethylbut*-1-*ene* (9e);[11] $v_{max.}$(CCl₄) 3 060 and 1 635 cm⁻¹ (CH=C); δ_H(CCl₄) 1.0, 1.1 (6 H, 2 t, *J* 7 Hz, 2 × CH₃), 2.1, 2.2 (4 H, 2 q, *J* 7 Hz, 2 × CH₂), and 5.7 (1 H, s, CHCl); δ_C(neat) 11.0, 11.8 (2 × CH₃), 23.0, 27.2 (2 × CH₂), 111.2 (CHCl), and 145.9 (C=CCl); *m/z* 120 (*M⁺* + 2, 33%), 118 (*M⁺*, 100), 103 (12), 91 (25), 89 (75), 83 (48), 82 (11), (78 (12), 77 (15), 76 (33), 75 (28), 69 (25), 63 (94), 65 (29), 63 (12), 56 (20), 55 (89), 54 (12), 53 (84), 51 (36), 50 (21), 41 (55), and 39 (49).

1,1-*Dibromo*-2-*ethylbut*-1-*ene* (8f) (Found: C, 29.5; H, 3.9. $C_6H_{10}Br_2$ requires C, 29.79; H, 4.17%); $v_{max.}$(CCl₄) 1 615 cm⁻¹ (C=C); δ_H(CCl₄) 0.95 (6 H, t, *J* 7 Hz, 2 × CH₃), and 2.25 (4 H, q, *J* 7 Hz, 2 × CH₂); δ_C(CCl₄) 12.5 (2 × CH₃), 30.1 (2 × CH₂), 87.0 (CBr₂), and 149.9 (C=CBr₂); *m/z* 244 (*M⁺* + 4, 50%), 242 (*M⁺* + 2, 99), 240 (*M⁺*, 50), 227 (12), 215 (47), 213 (95), 211 (48), 202 (46), 200 (94), 199 (11), 198 (50), 163 (21), 161 (22), 135 (24), 134 (12), 133 (72), 132 (12), 131 (54), 121 (27), 119 (43), 117 (16), 107 (13), 82 (15), 81 (100), 80 (11), 79 (68), 77 (18), 68 (22), 66 (30), 65 (52), 56 (76), 55 (17), 53 (60), 52 (19), 51 (64), 50 (31), 41 (40), 39 (51), and 38 (13).

1-*Bromo*-2-*ethylbut*-1-*ene* (9f) (Found: C, 43.9; H, 6.5. $C_6H_{11}Br$ requires C, 44.20; H, 6.80%); $v_{max.}$(CCl₄) 3 030 and 1 620 cm⁻¹ (CH=C); δ_H 1.0, 1.05 (6 H, 2 t, *J* 7 Hz, 2 × CH₃), 2.15, 2.25 (4 H, q, *J* 7 Hz, 2 × CH₂), and 5.7 (1 H, s, CHBr); δ_C(CCl₄) 11.5, 12.3 (2 × CH₃), 26.0, 28.7 (2 × CH₂), 100.8 (CHBr), and 148.2 (C=CBr); *m/z* 164 (*M⁺* + 2, 43%), 162 (*M⁺*, 44), 135 (15), 133 (16), 83 (48), 67 (24), 55 (100), 53 (24), 41 (20), and 39 (12).

Bromochloromethylenecyclohexane (8g) (Found: C, 39.8; H, 4.5. $C_7H_{10}BrCl$ requires C, 40.13; H, 4.81%); $v_{max.}$(film) 1 610 cm⁻¹ (C=C); δ_H(CCl₄) 1.5—1.7 [6 H, m, (CH₂)₃CH₂C=C] and 2.4—2.6 (4 H, m, 2 × CH₂C=C); δ_C(CCl₄) 26.4 [CH₂(CH₂)₂C=C] 27.1 (2 × CH₂CH₂C=C), 32.4, 36.0 (2 × CH₂C=C), 98.3 (CBrCl), and 142.2 (C=CBrCl); *m/z* 212 (*M⁺* + 4, 14%), 210 (*M⁺* + 2, 56), 208 (*M⁺*, 44), 170 (12), 168 (47), 166 (37), 129 (12), 100 (11), 93 (94), 91 (49), 89 (11), 87 (25), 79 (13), 77 (44), 75 (12), 73 (17), 68 (100), 67 (32), 65 (32), 63 (14), 55 (12), 51 (26), 50 (10), 41 (10), and 39 (23).

Chloromethylenecyclohexane (9g);[13] $v_{max.}$(CCl₄) 3 050 and 1 610 cm⁻¹ (CH=C); δ_H(CDCl₃) 1.4—1.6 [6 H, m, (CH₂)₃CH₂C=C], 2.0—2.3 (4 H, m, 2 × CH₂C=C), and 5.7 (1 H, s, CHCl); δ_C(CCl₄) 27.0, 27.5, 29.0, 29.5, 35.0 (5 × CH₂), 110.0 (CHCl), and 143.0 (C=CCl); *m/z* 132 (*M⁺* + 2, 13%), 130 (*M⁺*, 42), 95 (45), 90 (13), 88 (38), 81 (100), 79 (33), 77 (16), 68 (38), 67 (46), 65 (17), 55 (12), 53 (24), 51 (10), and 39 (18).

Dibromomethylenecyclohexane (8h);[14] $v_{max.}$(CCl₄) 1 620 cm⁻¹ (C=C); δ_H(CDCl₃) 1.4—1.7 [6 H, m, (CH₂)₃CH₂C=C] and 2.2—2.7 (4 H, m, 2 × CH₂C=C); δ_C(CCl₄) 25.9 [CH₂(CH₂)₂C=C], 26.5 (2 × CH₂CH₂C=C), 34.6 (2 × CH₂C=C), 82.9 (CBr), and 145.3 (C=CBr₂); *m/z* 256 (*M⁺* + 4, 5%), 254 (*M⁺* + 2, 13), 252 (*M⁺*, 7), 214 (15), 212 (33), 210 (17), 133 (14), 131 (16), 119 (15), 117 (12), 94 (13), 93 (92), 91 (43), 79 (18), 77 (37), 68 (100), 67 (34), 65 (25), 63 (10), 55 (10), 51 (19), and 39 (20).

Bromomethylenecyclohexane (9h);[15] $v_{max.}$(CCl₄) 3 050 and 1 610 cm⁻¹ (CH=C); δ_H(CDCl₃) 1.4—1.6 [6 H, m, (CH₂)₃CH₂C=C], 2.0—2.2 (4 H, 2 m, 2 × CH₂C=C), and 5.7 (1 H, s, CHBr); δ_C(CCl₄) 22.0, 22.5, 24.0, 27.0, 31.7 (5 × CH₂), 94.0 (CHBr), and 140.5 (C=CBr); *m/z* 176 (*M⁺* + 2, 21%), 174 (*M⁺*, 21), 134 (10), 132 (11), 95 (100), 79 (11), 67 (32), 53 (11), and 39 (10).

Dichloromethylenecyclohexane (8i);[7] $v_{max.}$(film) 1 615 cm⁻¹ (C=C); δ_H(CCl₄) 1.4—1.6 [6 H, m, (CH₂)₃CH₂C=C] and 2.2—2.5 (4 H, m, CH₂C=C); δ_C(neat) 26.5 [CH₂(CH₂)₂C=C], 27.6 (2 × CH₂CH₂C=C), 32.5 (2 × CH₂C=C), 112.3 (CCl₂), and 139.1 (C=CCl₂); *m/z* 168 (*M⁺* + 4, 3%), 166 (*M⁺* + 2, 13),

164 (M^+, 21), 124 (21), 122 (33), 93 (18), 91 (11), 87 (15), 81 (18), 77 (11), 68 (100), 67 (24), 65 (10), and 55 (13).

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