Chromium(II) Reduction of Trichloromethyl Carbinols and their Corresponding Ethers: One-step Synthesis of *Z*-Vinyl Chlorides

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Secondary trichloromethyl carbinols and their corresponding ethers can be reduced by chemically or electrochemically generated chromium(II) chloride to form *Z*-monochlorovinyl compounds in one step. In the presence of a carboxy function in the α-position an *E*-double bond is formed. Tertiary carbinols favour the formation of dichlorovinyl compounds and rearranged carbonyl compounds. Product ratios can be altered drastically by a change in the reaction conditions; this sheds light on the reaction mechanism.

Trichloromethyl carbinols and their ethers represent a large class of compounds of great structural variety which are easily accessible by numerous synthetic pathways. The latter include, for example, aldol reactions between chloral and a second carbonyl compound,[1,2] addition of the chemically[3] or electrochemically[4] generated trichloromethyl anion to carbonyl compounds, or proton or Lewis acid-catalysed addition of chloral to alkenes.[5,6,7] The reduction of trichloromethyl carbinols and their ethers can be performed electrochemically[4,5,8] or with zinc dust,[9] usually *via* the intermediate acetates, in strongly acidic media. All such procedures lead solely to the 1,1-dichlorovinyl compounds and in addition have several drawbacks. The reduction with zinc dust is connected with the formation of environmentally hazardous zinc salts and the substrates have to be acylated in an additional step.

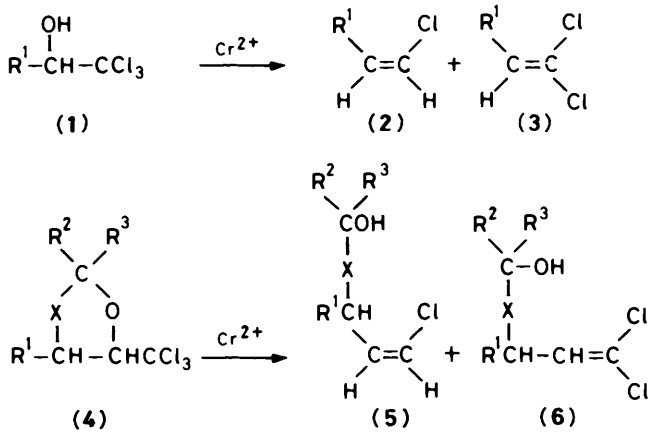
Chromium(II) salts are very useful reducing agents with a wide applicability in organic synthesis.[10] We have intensively studied electrochemical *in situ* regeneration of chromium(II) reagents for the reductive coupling of allyl and benzyl halides,[11] the dehalogenation of β-hydroxy halides,[12] the preparation of allenes,[13] and the reduction of activated acetylenes.[14] It was, therefore, of great interest to study the reduction of trichloromethyl carbinols by electrochemically or chemically generated chromium(II) which has not previously been investigated.

Results and Discussion

The trichloromethyl carbinols and ethers were reduced in the absence of oxygen by the addition of the substrate (1 equiv.) in a little dimethylformamide, to 4.2 equivalents of a 1:1 mixture of DMF and a 2 molar aqueous solution of $CrCl_2$ at 0 °C. The pH of the solution was *ca.* 3.5. The mixture was stirred for 2—16 h when g.l.c. or t.l.c. indicated the absence of starting substrate; the products were then isolated. If the substrates were sufficiently soluble in water, the reactions could also take place in this as a medium; such was the case for compounds (**1d**), (**1g**), (**7b**), and (**7c**).

The chromium(II) chloride reagent was prepared either by reduction of chromium(III) chloride with Zn–Hg or by electrochemical reduction. The latter was easily possible in a divided cell using a lead cathode with an acidic catholyte which afforded the reagent in 90% current yield. After ex-cell reduction of the substrates, the aqueous solution of the reagent could be recovered and regenerated electrochemically. In some cases continuous electrochemical in-cell regeneration of chromium(II) was possible.

It was found that under the conditions described above chromium(II) chloride reduced secondary trichloromethyl carbinols (**1**) and their corresponding ethers (**4**) to give largely the *Z*-monochlorovinyl compounds (**2**) and (**5**). In some cases, the dichlorovinyl compounds (**3**) and (**6**) were formed as side products (Scheme 1, Table 1). Not only are there few other methods for the selective preparation of *Z*-vinyl chlorides [*e.g.* the chlorination of (*E*)-vinylboronic acids[15] or the reaction of α-halogeno substituted allylsilanes with electrophiles[16]] but the starting materials are less accessible than the trichloromethyl carbinols.



Compd.	R^1	R^2	R^3	X
(**1a**), (**2a**)	2-Oxocyclohexyl	—	—	—
(**1b**), (**2b**)	PhCOCHMe	—	—	—
(**1c**), (**2c**), (**3c**)	Ph	—	—	—
(**1d**), (**2c**), (**3c**)	CH_2=CMeCH$_2$	—	—	—
(**1e**), (**2e**)	2-Methylcyclohex-2-enyl	—	—	—
(**1f**), (**2f**)	Cyclo-oct-2-enyl	—	—	—
(**1g**), (**2g**)	CO_2H	—	—	—
(**4a**), (**6a**)	H	-O-		—
(**4b**), (**5b**)	H	H	H	MeC=CMe
(**4c**), (**5c**), (**6c**)	$-CH_2(CH_2)_4CH_2-$		H	—
(**4d**), (**5d**)	$-CH_2(CH_2)_3CH_2-$		H	$-CH_2-$

Scheme 1.

Compounds (**1e—g**) and (**4a**) are exceptions. Thus trichlorolactic acid (**1g**) on reduction gave (*E*)-chloroacrylic acid (**2g**) as the sole product; this result is explained later. The low isolated yield of the acid (**2g**) is due to the poorness of its extraction from the aqueous solution, analytical results showing an actual yield of >60%. In the case of compound (**1e**) the *Z*-vinyl chloride (36%) is accompanied by the rearranged carbonyl compound 1-(2-methylcyclohex-2-enyl)ethanone (42%). Formation of the

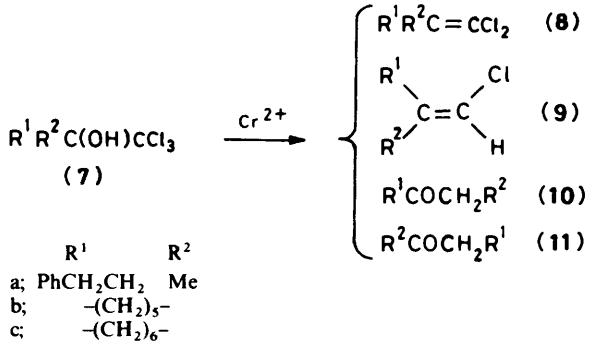
Table 1. Results of the reduction of secondary trichloromethyl carbinols and their ethers by chromium(II)[a]

Substrate	Products (%) (2)	(3)	(5)	(6)
(1a)	88	—		
(1b)	62	—		
(1c)[b]	44	10		
(1d)	60	10		
(1e)[c]	36	—		
(1g)	30[d]			
(4a)			—	80
(4b)			74	—
(4c)			60	15
(4d)			71	—

[a] In DMF–H_2O by addition of the substrate to $CrCl_2$ 4.2 (equiv.) at pH 3.5. [b] Acetophenone (3%) and phenylacetaldehyde (8%) as side products. [c] 1-(2-Methylcyclohex-2-enyl)ethanone was the major product (42%). [d] Product of *E*-configuration; isolated yield. Actual yield was higher, however the product was not totally isolable

latter compounds may be suppressed by a lowering of the reaction temperature and the pH. Compound (**1f**) leads mainly to the hydrolysis product of the dichlorovinyl compound (**3f**), cyclo-oct-2-enylacetic acid, in 50% yield, accompanied by 15% of the *Z*-vinyl chloride (**2f**) and 25% of both the rearranged carbonyl compounds. 4-Trichloromethyloxetan-2-one (**4a**) forms the dichlorovinylacetic acid (**6a**) as the only product in excellent yield. This compound can also be obtained by direct cathodic reduction.[8]

Tertiary trichloromethyl carbinols (**7**) give mainly the dichlorovinyl compounds (**8**), accompanied by the monochlorovinyl (**9**) and the rearranged carbonyl compounds (**10**) and (**11**) (Scheme 2, Table 2). The tendency of tertiary trichloromethyl



Scheme 2.

carbinols to form predominantly the dichlorovinyl and rearranged carbonyl compounds is borne out by the reduction of 2-trichloromethylpropan-2-ol to give 1-chloro-2-methylprop-1-ene, 1,1-dichloro-2-methylprop-1-ene, and butan-2-one in 15, 60 and 20% yield respectively. Using compound (**7b**) as a model it has been demonstrated that low temperature, low pH, and low chromium(II) concentration favours the formation of the dichlorovinyl compounds over the carbonyl compounds.

Preparative reduction of compounds (**7b**) and (**7c**) at pH 1, 0 °C, using a substrate:chromium(II) ratio of 1:4.2, yielded the dichlorovinyl compounds (**8b**) and (**8c**) in 80 and 77% yield respectively, the formation of the carbonyl compounds (**10b**)

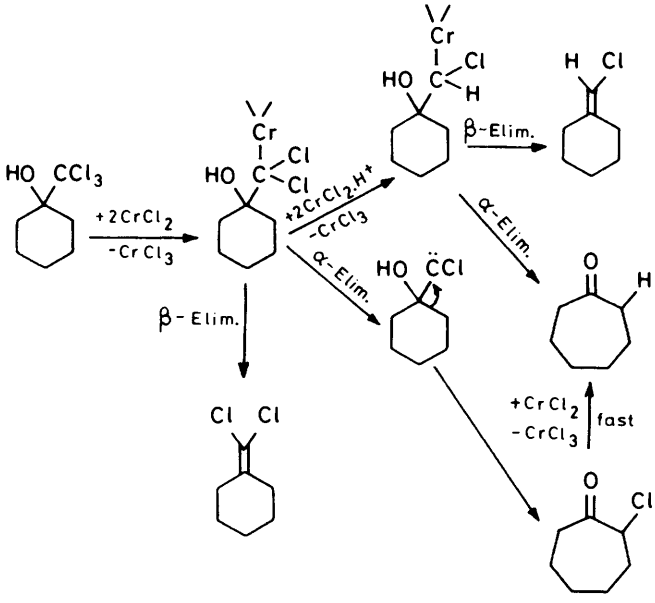
Table 2. Results of the reduction of tertiary trichloromethyl carbinols by chromium(II)[a]

Substrate	Products (%) (8)	(9)	(10)	(11)
(7a)	56	13	14	10
(7b)	63	11	17	
(7b)[b]	80	14		
(7c)	45	22	25	
(7c)[b]	77	8		

[a] In DMF–water by addition of the substrate to $CrCl_2$ (4.2 equiv.) at pH 3.5. [b] In water at pH 1 and 0 °C by addition of the reagent to the substrate.

and (**10c**) being totally suppressed. With compounds (**1c**), (**1d**), (**1f**), (**4b**), and (**4d**) reduction of the trichloromethyl carbinol function gave the corresponding acetylenes in yields of 1—9% as side products.

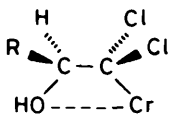
By analogy and on the basis of the experimental results obtained the mechanism of the reaction is deduced as that shown in Scheme 3. We presume that initially halogen transfer[17]



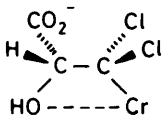
Scheme 3.

occurs with formation of an organodichlorochromium species and this, by β-elimination, yields the dichlorovinyl compound. Since elimination of the hydroxy group is favoured under the strongly acidic conditions which prevail, predominant formation of dichlorovinyl compounds from tertiary alcohols is understandable. At higher temperatures and pH values α-elimination is able to compete with β-elimination and this, after carbene insertion,[18] leads to the α-chlorocarbonyl compound. The latter is unstable under the reaction conditions and is reduced immediately to the carbonyl compound. Further reduction of the organodichlorochromium species could lead to organomonochlorochromium intermediates which, after β-elimination, would give the monochlorovinyl compound: this reaction path predominates with secondary carbinols and ethers.

We presume that selective formation of the *Z*-vinyl chlorides is a consequence of the conformation of the organodichlorochromium species which is fixed by chelation between the chromium centre and the β-hydroxy group [structure (**12**)]. In



(12)



(13)

the ensuing reduction step the chromium(II) reagent will then attack from the less hindered side leading to the *Z*-alkene after β-elimination.

The formation of *E*-chloroacrylic acid from trichlorolactic acid can also be explained by the chelating effect of the β-hydroxy group during the formation of the dichlorochromium organic species [structure (**13**)]. The only difference is that in the following reduction step the chromium(II) reagent will be complexed by the carboxylate function and will, therefore, attack the chlorine atom on that side of the molecule.

Experimental

General.—The products were analysed and separated by spectroscopic and chromatographic methods. ^{1}H N.m.r. spectra were recorded on Varian EM-360, Bruker WH-90, and Bruker WM-400 spectrometers. ^{13}C N.m.r. spectra were recorded on Bruker WH-90 and WM-400 spectrometers. I.r. spectra were determined with Perkin-Elmer 177 and Pye Unicam SP 1100 instruments. Mass spectra were recorded on Varian MAT 111, A.E.I. MS-30, and MS-50 instruments. For g.l.c.–M.S. coupling, a Varian 1440 gas chromatograph in combination with a Varian MAT 111 mass spectrometer was used. Liquid chromatography was performed on silica gel 63/100 mesh (Merck) on glass columns, 5 cm (diam.) 20 cm, and 3 cm (diam.), and 35 cm. Gas-liquid chromatography was performed with Varian 2740 and Carlo Erba Fractovap 4100 instruments using the following glass columns: 2.2 mm (diam.), 2 m, 2% FFAP on Chromosorb W; 2.2 mm (diam.) 1 m, 12% SE 30 on Chromosorb W; 2.2 mm (diam.), 2 m, 4% SE30 on Chromosorb W; 2.2 mm (diam.), 2 m, 3% OV 101 on Chromosorb W.

Trichloromethyl Carbinols and Ethers (**1**).—Compounds (**4a**), (**1d**), and (**1g**) were kindly supplied by BASF Aktiengesellschaft, Ludwigshafen. All other compounds were prepared according to literature procedures.[1,2,3,5,6]

2-(2,2,2-*Trichloro*-1-*hydroxyethyl*)*cyclohexanone* (**1a**).—This compound was prepared by an aldol reaction according to the literature.[1] Physical and spectroscopic data compared well with those reported.

4,4,4-*Trichloro*-3-*hydroxy*-2-*methyl*-1-*phenylbutan*-1-*one* (**1b**).—This compound was prepared by an aldol reaction in an analogous way to that described in the literature,[2] m.p. 125—126 °C (from cyclohexane) (Found: C, 46.8; H, 3.95; Cl, 37.75. $C_{11}H_{11}Cl_3O$ requires C, 46.92; H, 3.94; Cl, 37.77); $\nu_{max.}$(KBr) 3 450s (OH), 1 680s (C=O), 1 600, 1 585m, 815, 800, 790s (CCl_3), 765m, 720m, 685w, and 665w cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.41 (3 H, d, ^3J 7 Hz, Me), 3.4—3.7 (1 H, d, ^3J 4 Hz, OH, disappears with D_2O), 4.19 (1 H, dq, ^3J 5, 7 Hz, CHMe), 4.7—5.0 (1 H, m, C*H*OH), 7.4—7.8 (3 H, m, ArH), and 7.9—8.2 (2 H, m, ArH); δ_C (90 MHz; $CDCl_3$) 14.66 (q, Me), 42.63 (d, *C*HMe), 81.31 (d, CHOH), 103.32 (s, CCl_3), 128.66 (d, ArC), 128.95 (d, ArC), 133.68 (d, ArC), 135.36 (s, ArC), and 202.14 (s, C=O); *m/z* 105 (100%), 77 (26), 106 (7.8), 134 (3), 133 (3), and 163 (1, *M* − CCl_3).

Compounds (**1c**), (**7b**), *and* (**7c**).—These compounds were prepared from the carbonyl compounds and chloroform according to the literature.[3] Physical and spectroscopic data compared well with those reported.

1,1,1-*Trichloro*-2-*hydroxy*-2-*methyl*-4-*phenylbutane* (**7a**).—The trichloride (**7a**) was prepared from 4-phenylbutan-2-one and chloroform in an analogous way to that described in the literature,[3] m.p. 34—35 °C (from pentane) (Found: C, 49.55; H, 4.95. $C_{11}H_{13}Cl_3O$ requires C, 49.37; H, 4.90); $\nu_{max.}$(film) 3 600, 3 500s (OH), 3 115w, 3 095w, 3 060m, 3 015w, 2 995m, 2 975m, 2 895m, 2 000—1 600 (4 broad signals), 1 610m, 1 500m, 1 460s, 1 380m, 1 270m, 1 220m, 1 135m, 1 075m, 1 035m, 985, 970m, 920m, 845, 830, 800s (CCl_3), 750m, 705m, and 655m cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.63 (3 H, s, Me), 2.0—3.1 (4 H, m, CH_2CH_2, AA′—BB′) 2.43 (1 H, s, OH, disappears with D_2O), and 7.25 (5 H, s, ArH); δ_C (90 MHz; $CDCl_3$) 21.30 (q, Me), 30.62 (t, CH_2), 37.61 (t, CH_2Ar), 82.73 (s, COH), 109.82 (s, CCl_3), 126.10 (d, ArC), 128.40 (d, ArC), 128.52 (d, ArC), and 141.45 (s, ArC); *m/z* 266, 268, 270, 272 (*M*$^+$, 3.3, 3.1, 1.0, 0.1%), 91 (100), 149 (42), 125, 127 (33, 12), 104 (28), 105 (24), 43 (24), 92 (16), 65 (15), and 131 (14).

5,6-*Dihydro*-3,4-*dimethyl*-6-*trichloromethyl*-2H-*pyran* (**4b**).—The pyran (**4b**) was prepared from 2,3-dimethylbuta-1,3-diene and chloral* using $AlCl_3$ as the catalyst,[5,6] b.p. 80—85 °C/1 mmHg (lit.,[19] 99—100 °C/4.5 mmHg); $\nu_{max.}$(film) 3 000, 2 950, 2 880, 2 850, 1 455, 1 125, 1 040, 800, and 700 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.58 (3 H, m, Me), 1.71 (3 H, m, Me), 2.2—2.5 (2 H, m, CH_2), 4.04 (1 H, dd, ^3J 5, 9 Hz, $CHCCl_3$), and 4.1—4.3 (CH_2O, m); δ_C (90 MHz; $CDCl_3$) 13.56 (q, Me), 18.42 (q, Me), 31.91 (t, CH_2), 70.82 (t, CH_2O), 83.99 (d, CH), 100.34 (s, CCl_3), 122.19 (s, C=), and 124.03 (s, C=); *m/z* 228, 230, 232, 234 (*M*$^+$, 13, 13, 4, 1%), 111 (100, *M* − CCl_3), 83 (40), 55 (38), 41 (44), 43 (41), 39 (21), 67 (15), 213, 215, 217, and 219 (6, 5, 0.3, 0.1, *M* − Me).

6-(2,2,2-*Trichloro*-1-*hydroxyethyl*)-1-*methylcyclohex*-1-*ene* (**1e**).—Cyclohexene (**1e**) was prepared by an $AlCl_3$-catalysed reaction from 1-methylcyclohexene and chloral by a literature procedure.[7] Two diastereoisomers were formed in a ratio of 8:1, together with small amounts of the *exo*-methylene isomer, b.p. 120—123 °C/1.5 mmHg (mixture of diastereoisomers) (lit.,[7] 82—85 °C/1 mmHg); i.r. and ^{1}H-n.m.r. spectra compared well with literature data;[7] δ_C (90 MHz; $CDCl_3$; isomer 1) 22.0 (q, Me), 20.9 (t, CH_2), 22.5 (t, CH_2), 25.0 (t, CH_2), 40.8 (d, CH), 82.1 (d, CHOH), 103.8 (s, CCl_3), 127.6 (d, –CH=), and 132.2 (s, –C=); δ_C (90 MHz; $CDCl_3$; isomer 2) 22.0 (q, Me), 17.3 (t, CH_2), 25.2 (t, CH_2), 30.0 (t, CH_2), 40.6 (d, CH), 86.1 (d, CHOH), 114.1 (s, CCl_3), 128.2 (d, –CH=), and 131.8 (s, –C=); *m/z* 242, 244 (*M*$^+$, 0.64, 0.66%), 95 (100), 67 (10), 55 (9), 81 (9), 36 (8), 96 (7), 79 (7), and 41 (6) (Found: *M*$^+$, 244.0008. $C_9H_{13}{}^{35}Cl_2{}^{37}ClO$ requires *M*, 244.0003; Found: *M*$^+$, 242.0041. $C_9H_{13}{}^{35}Cl_3O$ requires *M*, 242.0032).

3-(2,2,2-*Trichloro*-1-*hydroxyethyl*)*cyclo*-*oct*-1-*ene* (**1f**) *and* 9-*Trichloromethyl*-8-*oxabicyclo*[5.2.1]*decane* (**4d**).—These compounds were prepared by an $AlCl_3$-catalysed reaction from cyclo-octene and chloral.[5,6] The structure of (**4d**) was determined by 2D-n.m.r. (COSY, INADEQUATE) and is analogous to the product of the chloral–cyclohexene reaction.[20] Compound (**1f**) and (**4d**) were separated by liquid chromatography on silica gel with cyclohexane–dichloromethane (1:1) to yield (**1f**) (25%), whose i.r. and ^{1}H n.m.r. spectra compared well with literature data;[7] δ_C (90 MHz; $CDCl_3$) 25.0 (t, CH_2), 27.2 (t, CH_2), 27.4 (t, CH_2), 29.7 (t, CH_2), 35.4 (t, CH_2), 37.0 (d, CH), 85.84 (d, CHOH), 104 (s, CCl_3), 126.6 (d, CH=), and 130.6 (d, CH=); *m/z* 256, 258, 260, 262 (*M*$^+$, 1.8, 1.6, 0.4, 0.1%), 67 (100), 109 (58), 41 (28), 55 (26), 79 (26), 121 (20), 93 (19), 81 (18), 57 (18), 139 (16), and 95 (14) (Found: C, 46.8; H, 5.9; Cl, 41.35. $C_{10}H_{15}Cl_3O$ requires C, 46.63; H, 5.87; Cl, 41.29%); and compound (**4d**) 25% $\nu_{max.}$(film) 2 960s, 2 890m, 1 480s, 1 455s,

* Chloral = trichloroacetaldehyde.

1 130s, 1 090s, and 820s cm^{-1}; δ_H (400 MHz; $CDCl_3$) 1.24 (1 H, m, 4α-H), 1.34—1.48 (2 H, m, 3α-H, 6α-H), 1.55—1.7 (2 H, m, 2α-H, 5α-H), 1.7—1.8 (2 H, m, 5β-H, 10α-H), 1.8—1.97 (3 H, m, 2β-H, 3β-H, 4β-H), 2.04 (1 H, m, 6β-H), 2.66 (1 H, m, 10β-H), 2.74 (1 H, m, 1-H), 4.44 (1 H, d, ^3J 1.7 Hz, CHO), and 4.70 (1 H, ddd, ^3J 3.2, 6.5, 10.0 Hz, $OCHCCl_3$); δ_C (90 MHz; $CDCl_3$) 26.1 (t, CH_2), 26.2 (t, CH_2), 27.5 (t, CH_2), 35.3 (t, CH_2), 35.4 (t, CH_2), 37.1 (t, CH_2), 40.6 (d, CH), 81.3 (d, CHO), 94.9 (d, $CHCCl_3$), and 103.4 (s, CCl_3); *m/z* 256, 258, 260 (M^+, 0.4, 0.4, 0.1%), 139 (100), 121 (70), 69 (37), 93 (35), 41 (35), 55 (31), 67 (29), 79 (28), 199, 201, 203, and 205 (9.4, 8.9, 2.9, 0.2) (Found: C, 46.8; H, 5.8; Cl, 41.35. $C_{10}H_{15}Cl_3O$ requires C, 46.63; H, 5.87; Cl, 41.29%).

10-*Trichloromethyl-9-oxabicyclo*[6.2.0]*decane* (**4c**).—The trichloride (**4c**) was prepared by the slow addition of $AlCl_3$ (0.7 g, 5.3 mmol) to a solution of cyclo-octene (57.3 g, 0.52 mol) and chloral (50.0 g, 0.34 mol) in dichloromethane (50 ml) at −3—5 °C. The mixture was stirred for 30 min and then hydrolysed by the addition of ice. After work-up according to the literature procedure,[5,6] a crude product was isolated (88.3 g). Vacuum distillation (105—110 °C/0.5 mmHg) afforded compounds (**4c**) and (**1f**) in a ratio of 85:15. Storage of the oily product at −18 °C caused crystallization of compound (**4c**) (58 g, 66%), m.p. 29—31 °C (Found: C, 46.5; H, 5.85; Cl, 41.45. $C_{10}H_{15}Cl_3O$ requires C, 46.63; H, 5.87; Cl, 41.29%); $\nu_{max.}$ 2 950s, 2 860w, 1 460s, 1 445s, 1 030s, 1 010m, 935s, and 830—730s, (several signals) cm^{-1}; δ_H (90 MHz; $CDCl_3$) 0.9—2.3 (12 H, m, CH_2), 2.66—3.03 (1 H, m, CH), 4.48 (1 H, d, ^3J 2.1 Hz, $CHCCl_3$), and 4.80 (1 H, ddd, ^3J 1.4, 4.5, 3.3 Hz, CHO); δ_C (90 MHz; $CDCl_3$) 25.76 (t, 2 CH_2), 26.06 (t, CH_2), 26.35 (t, CH_2), 28.52 (t CH_2), 30.04 (t, CH_2), 41.33 (d, CH), 82.93 (d, CHO), 91.92 (d, $CHCCl_3$), and 100.99 (s, CCl_3); *m/z* 98 (100%), 93 (81), 41 (90), 55 (77), 67 (76), 121 (69), 79 (64), 36, 38 (58, 17), 81 (49), 39 (45), 69 (37), 95 (37), 122, 124, 126 (32, 21, 3.4), 57 (30), and 139 (29, $M - CCl_3$). Similar formation of an oxetane derivative has been reported by Kwart.[21]

General Procedure for the Reduction of Trichloromethyl Carbinols by $CrCl_2$.—Equivalent amounts of DMF and 2M-aqueous $CrCl_2$ were mixed with exclusion of oxygen at 0 °C. The trichloromethylmethanol was added with stirring in such a way that $CrCl_2$ was present in a 4.2 molar excess and the pH of the solution was 3.5; the mixture was then stirred 2—16 h. The disappearance of substrate was monitored by g.l.c. or t.l.c. Work-up involved the addition of water and several extractions with n-pentane. The combined extracts were washed with aqueous sodium chloride, dried ($MgSO_4$), and evaporated and the crude product separated either by distillation or by chromatography on silica gel using dichloromethane–cyclohexane (1:0—1:1) as the eluant.

Chemical Procedure for the Formation of a $CrCl_2$ *Solution.*—A 2M-aqueous solution of $CrCl_3$ was treated with Zn–Hg. After complete reaction, as determined by titration, the reagent solution was used for the reactions.

Electrochemical Procedure for the Formation of a $CrCl_2$ *Solution.*—In a divided cell, separated by an anion exchange membrane and equipped with a lead cathode (99.995%), a platinum or lead dioxide anode, and a Ag–AgCl reference electrode, $CrCl_3 \cdot 6H_2O$ in 0.06M-HCl containing $CaCl_2$ (0.23M) as supporting electrolyte was electrolysed at a potential of −0.7 to −1.0 V with a current density of 30—50 mA cm^{-2}. Saturated aqueous NaCl was used as the anolyte. $CrCl_2$ was produced with a current yield of 92%.

Alternatively the cell was separated by a Nafion cation exchange membrane. Aqueous $CrCl_3 \cdot 6H_2O$ was used as the catholyte and 5% sulphuric acid as the anolyte. Electrolysis took place with a current density of 50 mA cm^{-2} without potential control. $CrCl_2$ was produced with a current yield of 85—90%.

In-cell Reduction of Trichloromethyl Carbinols by Electrogenerated $CrCl_2$.—Trichloromethylmethanols can be reduced continuously during electrochemical generation of $CrCl_2$ as described in the preceding section. This was demonstrated by the reduction of 4-trichloromethyloxetan-2-one (**4a**). After extraction of the product with dichloromethane, the catholyte could be used again for electrolysis: this procedure was thrice repeated. In the case of compound (**4a**) THF was used as a co-solvent instead of DMF.

Ex-cell Reduction of Trichloromethyl Carbinols by Electrogenerated $CrCl_2$.—The electrochemically generated $CrCl_2$ solution was added to the trichloromethyl carbinol dissolved in DMF. After the mixture had been stirred for 2 h it was worked up as described in the general procedure. The aqueous solution could be re-used for the electrogeneration of $CrCl_2$.

Reduction of Trichloromethyl Carbinols by a Chemically Generated $CrCl_2$ *Solution.*—(*a*) *Reduction of the methanol* (**1a**). According to the general procedure compound (**1a**) (4.51 g, 18.4 mmol) was treated with a 1.5M-$CrCl_2$ solution (55.2 ml, 82.8 mmol). Distillation of the crude product yielded (Z)-2-(2-*chlorovinyl*)*cyclohexanone* (**2a**) (2.55 g, 16 mmol, 88%), b.p. 60 °C/0.5 mmHg [Found (for the 2,4-dinitrophenylhydrazone derivative): C, 49.6; H, 4.35; N, 16.45. $C_{14}H_{15}ClN_4O_4$ requires C, 49.64; H, 4.46; N, 16.54]; $\nu_{max.}$(film) 3 120w, 3 060w, 2 960s, 2 880m, 1 720s (C=O), 1 640m (C=C), 1 450m, 1 430w, 1 360m, 1 330m, 1 315m, 1 300w, 1 225w, 1 135m, 1 095w, 1 075w, 960w, 920w, 890w, 865w, 840w, 795w, 730, and 720s (*cis* CH=CH); δ_H (90 MHz; $CDCl_3$) 1.2—2.6 (8 H, m, CH_2), 3.57 (1 H, m, CH), 6.04 (1 H, dd, ^3J 7.2, 7.2 Hz, CH=), and 6.18 (1 H, d, ^3J 7.2 Hz, CH=); δ_C (90 MHz; $CDCl_3$) 24.63 (t, CH_2), 27.55 (t, CH_2), 33.47 (t, CH_2), 41.63 (t, CH_2), 49.20 (d, CH), 119.24 (d, =CHCl), 129.05 (d, CH=), and 208.48 (s, C=O); *m/z* 158, 160 (M^+, 1.8, 0.5%), 79 (100), 123 (94), 114, 116 (49, 16), 67 (44), 39 (38), 88, 90 (38, 13), 41 (23), 65 (22), 70 (20), and 95 (20) (Found: *M*, 158.0496. $C_8H_{11}{}^{35}ClO$ requires *M*, 158.0499; Found: M^+, 160.0460. $C_8H_{11}{}^{37}ClO$ requires *M*, 160.0469).

(*b*) *Reduction of the carbinol* (**1b**). According to the general procedure compound (**1b**) (2.28 g, 8.1 mmol) was treated with a 1.39M-$CrCl_2$ solution (25 ml, 35 mmol). Liquid chromatography of the crude product on silica gel using dichloromethane as eluant (R_F = 0.8) yielded (Z)-4-*chloro*-2-*methyl*-1-*phenylbut*-3-*en*-1-*one* (**2b**) (0.97 g, 5.0 mmol, 62%), δ_H (90 MHz; $CDCl_3$) 1.28 (3 H, d, ^3J 7 Hz, Me), 4.63 (1 H, dq, ^3J 7, 8.8 Hz, CH), 5.89 (1 H, dd, ^3J 7, 8.8 Hz, CH=), 6.08 (1 H, d, ^3J 7 Hz, CH=) 7.2—7.7 (3 H, m, ArH) and 7.8—8.1 (2H, m, ArH); δ_C (90 MHz; $CDCl_3$) 16.83 (q, Me), 40.26 (d, CH), 119.15 (d, =CHCl), 128.53 (d, ArCH,), 128.73 (d, ArCH), 131.67 (d, CH=), 133.35 (d, ArCH), 135.94 (s, ArC), and 200.42 (s, C=O); *m/z* 194, 196 (M^+, 0.2, 0.06%), 105 (100), 77 (56), 51 (18), 106 (11), 53 (5), 80 (5), 50 (4), 39 (2) (Found: M^+, 194.0505. $C_{11}H_{11}{}^{35}ClO$ requires *M*, 194.0498; Found: M^+, 196.0455. $C_{11}H_{11}{}^{37}ClO$ requires *M*, 196.0469). The 2,4-dinitrophenylhydrazone derivative had m.p. 101—105 °C (from ethanol) (Found: C, 54.65; H, 4.0; N, 14.95. $C_{17}H_{15}ClN_4O_4$ requires C, 54.48; H, 4.03; N, 14.95%).

(*c*) *Reduction of the carbinol* (**1c**). According to the general procedure compound (**1c**) (2.4 g, 10.7 mmol) was treated with a 1.6M-$CrCl_2$ solution (28 ml, 44.8 mmol) and the product (**2c**) (0.65 g, 4.7 mmol, 44%) was isolated by vacuum distillation, b.p. 54—57 °C/5 mmHg (lit.[22] 54 °C/4 mmHg). The *Z*-configuration of the double bond was confirmed by ^1H n.m.r. spectroscopy: δ_H (90 MHz; $CDCl_3$) 6.20 (1 H, d, H_α) and 6.57 (1 H, d, *J* 8.1 Hz,

H_8) (lit,[23] 6.18, 6.55, *J* 8.0 Hz). Side-products (**3c**) (0.11 mmol, 10%), acetophenone, and phenylacetaldehyde were detected by g.l.c. and identified by comparison of their R_F values with those of authentic samples on two different columns (SE 30 and OV 101).

(*d*) *Reduction of the carbinol* (**1d**). According to the general procedure compound (**1d**) (5.16 g, 25.4 mmol) was treated with a 0.3M-$CrCl_2$ solution (300 ml, 92.4 mmol). Distillation yielded (*Z*)-1-*chloro*-4-*methylpenta*-1,4-*diene* (**2d**) (1.78 g, 15.24 mmol, 60%), b.p. 55 °C/72 mmHg (Found: M^+, 118.0362. $C_6H_9{}^{37}Cl$ requires *M*, 118.0363; Found: M^+, 116.0393. $C_6H_9{}^{35}Cl$ requires *M*, 116.0393); $\nu_{max.}$ 3 110 (m, =CH), 3 000, 2 950s, 1 660s (C=C), 1 640s (C=CCl), 1 450s, 1 380m, 1 340m, 1 315m, 1 275w, 1 230w, 1 130—1 000 (several broad bands), 900s (=CH_2), 755s (CCl), 710s cm^{-1} (CH=CH, *cis*); δ_H (90 MHz: $CDCl_3$) 1.75 (3 H m, Me), 2.93 (2 H, dd, ^3J 7.2 Hz (*Z*), ^4J 1.4 Hz, CH_2), 4.74 (2 H, m, =CH_2), 5.79 (1 H, dt, ^3J 7.2, ^3J 7.2 Hz, CH=), and 6.12 (1 H, dt, ^3J 7.2 Hz(*Z*), ^4J 1.4 Hz, ClCH=), δ_C (90 MHz; $CDCl_3$) 22.53 (q, Me), 35.36 (t, CH_2), 111.18 (t, CH_2=), 119.31 (d, ClCH=), 129.25 (d, CH=), and 142.84 (s, C=); *m/z* 116, 118 (M^+, 41, 14%), 81 (100), 41 (48), 39 (45), 79 (47), 65 (28), 53 (26), and 57 (20). 1,1-Dichloro-4-methylpenta-1,4-diene (**3d**) (0.39 g, 2.54 mmol, 10%) was isolated by distillation. Physical and spectroscopic data compared well with an authentic sample and literature data.[24]

(*e*) *Reduction of the carbinol* (**1e**). According to the general procedure compound (**1e**) (7.45 g, 30.6 mmol) was treated with a 1.8M-$CrCl_2$ solution (68 ml, 122.4 mmol). Liquid chromatography of the crude product on silica gel using dichloromethane–cyclohexane (1 : 1) as the eluant yielded (*Z*)-6-(2-*chlorovinyl*)-1-*methylcyclohexene* (**2e**) (R_F = 0.9), (1.7 g, 11 mmol, 36%) (Found: M^+, 156.0705. $C_9H_{13}{}^{35}Cl$ requires *M*, 156.0694); $\nu_{max.}$ 3 080w, (CH=), 1 660w (C=C), 1 640s (C=CCl), 1 440s, 1 325s, 960, 950w, 860m, 800m, 780, and 710s cm^{-1}; δ_H (60 MHz; CCl_4) 1.1—2.3 (9 H, m), 3.0—3.4 (1 H, m, =CCHC=), 5.3—5.5 (1 H, m, C*H*=CMe), 5.6 (1 H, dd, ^3J 5.0, 6.5 Hz CH=), and 6.0 (1 H, dd, ^3J 5.0, ^4J 0.5 Hz, ClCH=); *m/z* 156.158 (M^+, 37, 12%), 121 (100), 93 (98), 79 (72), 68 (67), 77 (44), 39 (40), and 91 (40). Also isolated was 1-(2-methylcyclohex-2-enyl)ethanone (1.78 g, 12.9 mmol, 42%) (R_F = 0.4) which was identified by comparison of the physical and spectroscopic data with those reported.[25]

(*f*) *Reduction of the carbinol* (**1f**). According to the general procedure compound (**1f**) (2.23 g, 8.6 mmol) was treated with a 2.55M-$CrCl_2$ solution (15 ml, 38.3 mmol). The crude product was dissolved in ether. After the addition of 50% aqueous NaOH and extraction of the non-polar components by ether, it was acidified with HCl and re-extracted with ether. The ether phase was dried ($MgSO_4$) and evaporated, and the addition of a small amount of n-pentane at low temperature caused crystallization to give *cyclo-oct*-2-*enylacetic acid* (0.72 g, 4.3 mmol, 50%) as white crystals, m.p. 41—45 °C (from pentane) (Found: C, 71.2; H, 9.85. $C_{10}H_{16}O_2$ requires C, 71.39; H, 9.59%); $\nu_{max.}$(KBr) 3 700—2 300br (OH), 1 705s (C=O), and 705m cm^{-1} (CH=CH); δ_H (90 MHz; $CDCl_3$) 1.0—2.6 (10 H, m, ring CH_2), 2.37 (2 H, d, ^3J 7.0 Hz, C$H_2$$CO_2H$), 2.6—3.25 (1 H, m, CH), 5.1—5.4 (1 H, dd, ^3J 8.5, 10.3 Hz, CH=), 5.5—5.9 (1 H, ddd, ^3J 7.4, 8.4, 10.3 Hz, CH=), and 8—11 (v br, 1 H, CO_2H, disappears with D_2O); δ_C (90 MHz; $CDCl_3$) 25.63 (t, CH_2), 26.61 (t, 2 C, determined by inverse gated decoupling experiments, 2 × CH_2), 29.39 (t, CH_2), 32.92 (d, CH), 36.06 (t, CH_2), 41.14 (t, CH_2), 130.51 (d, CH=), 132.71 (d, CH=), and 179.19 (s, CO_2H); *m/z* 168 (M^+, 4.2%), 41 (100), 67 (95), 55 (69), 108 (54), 81 (54), 39 (48), 54 (43), and 79 (41). Liquid chromatography on a silica gel column eluting first with dichloromethane and then with light petroleum (40—60 °C) yielded (*Z*)-3-(2-*chlorovinyl*)*cyclo-octene* (**2f**) (15%, determined by g.l.c.) (Found: C, 70.45; H, 8.95; Cl, 20.65. $C_{10}H_{15}Cl$ requires C, 70.37; H, 8.86; Cl, 20.77%); δ_H (90 MHz; $CDCl_3$) 5.93 (1 H, dd, ^3J 6.8, ^4J 0.8 Hz, ClCH=); δ_C (90 MHz; $CDCl_3$) 117.1 (ClCH=); *m/z* 170, 172 (M^+, 1.6, 0.1%), 67 (100), 79 (74), 41 (40), 82 (33), 88, 90 (32, 10), 77 (30), 39 (29), 135 (27), and 93 (24). Two rearranged carbonyl compounds were analysed as a mixture by g.l.c.–m.s., ^1H, and ^{13}C n.m.r. spectroscopy: 1-(cyclo-oct-2-enyl)ethanone identified by comparison of the ^1H n.m.r. spectrum with that reported;[26] δ_C (90 MHz; $CDCl_3$) 50.5 (d, CH), and 211.0 (s, C=O); *m/z* 152 (M^+, 21%), 43 (100), 67 (64), 109 (30), 41 (26), 137 (18), 55 (17), 39 (15), 81 (15), 79 (14), and 123 (10); and cyclo-oct-2-enylacetaldehyde, δ_H (90 MHz; $CDCl_3$) 9.6 (1 H, m, CHO); δ_C (90 MHz; $CDCl_3$) 203.1 (d, CHO); *m/z* 67 (100%), 41 (75), 81 (62), 79 (56), 39 (40), 55 (38), 107 (35), 108 (31, M − CH_3CHO), 93 (30), 82 (30), 95 (28), 110 (23), and 121 (22) (Found: M^+, 152.1204. $C_{10}H_{16}O$ requires *M*, 152.1202).

(*g*) *Reduction of the hydroxy acid* (**1g**). Compound (**1g**) (3.84 g, 20 mmol) in water (5 ml) was treated with a 1.82M-$CrCl_2$ solution (45 ml, 82 mmol) under an argon atmosphere. The reaction was worked up by the addition of concentrated HCl (6 ml) and NaCl. The aqueous solution was then extracted with ether, and the extract dried ($MgSO_4$), and evaporated to give a yellow-green oil (2.32 g). Continuous extraction with n-pentane and evaporation of the solvent gave (*E*)-3-chloropropenoic acid (**2g**) (0.64 g, 6 mmol, 30%) as a white solid. The physical and spectroscopic data compared well with literature values.[27]

(*h*) *Reduction of the lactone* (**4a**). A stirred solution of compound (**4a**) (18.9 g, 100 mmol) in tetrahydrofuran (500 ml) was treated with aqueous 0.53M-$CrCl_2$ (750 ml, 0.4 mol). After 2 h the solution was extracted with dichloromethane, and the extract dried, and evaporated to yield compound (**6a**) (11.9 g, 77 mmol, 77%), m.p. 38—40 °C (from pentane) (lit.,[22] 40—41 °C). I.r. and n.m.r. spectra compared well with those reported.[22]

(*i*) *Reduction of the cyclic ether* (**4b**). According to the general procedure compound (**4b**) (6 g, 25 mmol) was treated with a 1.0M-$CrCl_2$ solution (105 ml, 105 mmol). Liquid chromatography of the crude product using dichloromethane as the eluant yielded (2Z,5Z)-6-*chloro*-2,3-*dimethylhexa*-2,5-*dien*-1-*ol* (**5b**) (R_F 0.23) (3.1 g, 19.3 mmol, 74%) (Found: C, 59.88; H, 8.25; Cl, 22.15. $C_8H_{13}ClO$ requires C, 59.81; H, 8.16; Cl, 22.07); $\nu_{max.}$ 3 400br (OH) 3 100w (CH=C), 1 670w (C=C), 1 630m (C=CCl), 1 010s (CH_2OH), 770, 750m, and 700w cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.69 (3 H, m, ^5J 0.75 Hz, Me), 1.75 (3 H, m, ^5J 0.9 Hz, Me), 2.40 (1 H, s, OH disappears with D_2O), 3.04 (2 H, m, CH_2), 4.14 (2 H, q, ^5J 0.75 Hz, CH_2OH), 5.67 (1 H, dt, ^3J 7.1, 7.1 Hz, CH=), and 6.07 (1 H, dt, ^3J 7.1, ^4J 1.55 Hz, ClCH=); δ_C (400 MHz, $CDCl_3$) 16.71 (q, Me), 18.77 (q, Me), 31.83 (t, CH_2), 63.36 (t, CH_2OH), 118.31 (d, =CHCl), 129.67 (s, C=), and 129.90 (d, CH=); *m/z* 160, 162 (M^+, 0.39, 0.10%), 107 (100), 91 (41), 85 (38), 41 (26), 67 (24), 43 (23), 39 (20), 142, 144 (15.4, 4.9), and 145, 147 (4.1, 1.2) (Found: M^+, 162.0622. $C_8H_{13}{}^{37}ClO$ requires *M*, 162.0625; Found: M^+, 160.0653. $C_8H_{13}{}^{35}ClO$ requires *M*, 160.0655). The structure was determined on the basis of ^1H n.m.r. double resonance experiments, using the nuclear Overhauser effect (n.O.e.), and by selective decoupling and inverse gated decoupling in the ^{13}C n.m.r. spectrum. This showed that the ^{13}C signal at 129.67 p.p.m. is produced by two carbon atoms. The *Z*-configuration of the tetrasubstituted double bond was determined by an n.O.e. experiment. The *Z*-configuration of the vinyl chloride group was assigned on the basis of the ^1H coupling constants.

(*j*) *Reduction of the cyclic ether* (**4c**). According to the general procedure compound (**4c**) (1.99 g, 7.7 mmol) was treated with a 1.72M-$CrCl_2$ solution (18 ml, 30.9 mmol). Liquid chromatography on silica gel using dichloromethane as the eluant yielded (*Z*)-2-(2-*chlorovinyl*)-1-*hydroxycyclo-octane* (**5c**) (R_F 0.4) (0.87 g, 4.62 mmol, 60%) (Found: C, 63.4; H, 8.85. $C_{10}H_{17}ClO$ requires C, 63.65; H, 9.08%); $\nu_{max.}$(film) 3 400br (OH), 3 100w

(CH=), 1 660 (m, C=C), 1 475, 1 450s, 1 115, 1 035, 1000—970, 900, 805, and 760—710 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.2—2.1 (13 H, m), 2.9—3.3 (1 H, m, CH), 3.8—4.1 (1 H, m, CHO), 5.93 (1 H, dd, ^3J 7.0, 8.2 Hz, CH=), and 6.08 (1 H, d, J 7.0 Hz, ClCH=); δ_C (90 MHz; $CDCl_3$) 23.1 (t, CH_2), 26.2 (t, CH_2), 26.4 (t, CH_2), 27.1 (t, CH_2), 27.7 (t, CH_2), 33.1 (t, CH_2), 39.8 (d, CH), 72.3 (d, CHOH), 117.3 (d, ClCH=), and 134.8 (d, CH=); *m/z* 188 (M^+, 0.09%), 54 (100), 98 (96), 67 (94), 41 (69), 88, 90 (62, 19), 79 (57), 55 (55), and 57 (55).

Also isolated was 2-(2,2-*dichlorovinyl*)-1-*hydroxycyclo-octane* (**6c**) (R_F 0.45) (0.26 g, 1.15 mmol, 15%) (Found: C, 53.85; H, 7.25. $C_{10}H_{16}Cl_2O$ requires C, 53.97; H, 7.34%); δ_H (90 MHz; $CDCl_3$) 1.2—2.1 (13 H, m), 2.7—3.0 (1 H, m, CH), 3.8—4.0 (1 H, m, CHO), and 6.07 (1 H, d, ^3J 9.5 Hz, CH=); δ_C (90 MHz; $CDCl_3$) 22.8 (t, CH_2), 26.0 (t, CH_2), 26.4 (t, CH_2), 26.9 (t, CH_2), 27.6 (t, CH_2), 33.3 (t, CH_2), 42.8 (d, CH), 72.2 (d, CHOH), 119.6 (s, Cl_2C=), and 132.8 (d, CH=); *m/z* 222, 224, 226 (M^+, 17.3, 11.1, 1.73%), 122, 124, 126 (100, 61, 10), 82 (56), 67 (55), 98 (48), 57 (45), 41 (36), and 95 (30) (Found: M^+, 222.0578. $C_{10}H_{16}{}^{35}Cl_2O$ requires M, 222.0578; Found: M^+, 224.0543. $C_{10}H_{16}{}^{35}Cl^{37}ClO$ requires M, 224.0548).

(*k*) *Reduction of the cyclic ether* (**4d**). According to the general procedure compound (**4d**) (0.86 g, 3.3 mmol) was treated with a 1.48M-$CrCl_2$ solution (9 ml, 13.4 mmol). Liquid chromatography on silica gel using dichloromethane as the eluant yielded (Z)-3-(2-*chlorovinyl*)-1-*hydroxycyclo-octane* (**5d**) (R_F 0.5) (0.42 g, 2.2 mmol, 67%; 71% with regard to turnover) (Found: C, 63.75; H, 9.2. $C_{10}H_{17}ClO$ requires C, 63.65; H, 9.08); $\nu_{max.}$ 3 400br (OH), 3 100w (CH=), 1 630s (C=C), 1 475, 1 450s (CH_2), 1 330m, 1 075m, 1 015s, 970m, 750s (CCl), and 720s (CH=CH, *cis*); δ_H (90 MHz; $CDCl_3$) 1.2—2.2 (12 H, m, CH_2), 2.2 (1 H, s, OH, disappears with D_2O), 2.6—3.0 (1 H, m, CH), 3.7—4.1 (1 H, m, CHO), 5.65 (1 H, dd, ^3J 7.2, 8.7 Hz, CH=), and 5.87 (1 H, dd, ^3J 7.2, ^4J 0.7 Hz, ClCH=); δ_C (90 MHz; $CDCl_3$) 21.8 (t CH_2), 23.5 (t, CH_2), 27.6 (t, CH_2), 32.3 (t CH_2), 33.9 (d, CH), 35.6 (t, CH_2), 40.5 (t, CH_2), 71.9 (d, CHOH), 115.5 (d, ClCH=), and 138.1 (d, CH=); *m/z* 188, 190 (M^+, 0.09, 0.01%), 135 (100), 67 (74), 88, 90 (61, 19), 41 (41), 57 (40), 93 (40), 81 (38), and 117 (33) (Found: M^+, 188.0961. $C_{10}H_{17}{}^{35}ClO$ requires M, 188.0967).

Reduction of the carbinol (**7a**). According to the general procedure compound (**7a**) (2.67 g, 10 mmol) was treated with a 1.9M-$CrCl_2$ solution (25 ml, 47 mmol). Bulb-to-bulb distillation yielded two products which were contaminated by small amounts of side products. Separation was achieved by liquid chromatography on silica gel eluting first with dichloromethane and then with light petroleum (40—60 °C) to give 1,1-*dichloro*-2-*methyl*-4-*phenylbut*-1-*ene* (**8a**) (1.2 g, 5.6 mmol, 56%), b.p. 120—128 °C/18 mmHg (partial decomposition) (Found: C, 61.6; H, 5.6; Cl, 32.55. $C_{11}H_{12}Cl_2$ requires C, 61.42; H, 5.62; Cl, 32.96%); $\nu_{max.}$ 3 140—2 890m, 1 960, 1 885, 1 850, 1 755wbr, 1 630m, 1 610m, 1 590w, 1 500m, 1 460m, 1 380w, 1 175, 1 165w, 1 090w, 1 060, 1 040w, 905s, 830w, 770w, 765m, and 705s cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.87 (3 H, s, Me), 2.42—3.89 [16 lines, m, 4 H, AA'BB', $(CH_2)_2$], and 7.24 (5 H, m, ArH); δ_C (90 MHz; $CDCl_3$) 20.10 (q, Me), 33.21 (t, CH_2), 37.51 (t, CH_2), 115.10 (s, Cl_2C=), 126.20 (d, ArCH), 128.37 (d, ArCH), 128.50 (d, ArCH), 134.52 (s, C=), and 140.96 (s, ArC); *m/z* 214, 216, 218 (M^+, 2.4, 1.8, 0.3%), 91 (100), 65 (20), 39 (15), 51 (13), 92 (8), 179, 181 (7, 2), 63 (5), 77 (5), 143 (4), 178, and 180 (4, 1, M^+ − HCl). The structure of the side product 1-chloro-2-methyl-4-phenylbut-1-ene (**9a**) was determined on the basis of the spectroscopic data as a mixture of *E*- and *Z*-isomers (0.23 g, 1.3 mmol, 13%) (Found: C, 73.2; H, 7.5. $C_{11}H_{13}Cl$ requires C, 73.13; H, 7.25%); δ_H (90 MHz; $CDCl_3$) 1.67 (3 H, d, ^4J 1.5 Hz, Me), 1.75 (3 H, d ^4J 1.46 Hz, Me), 5.69—5.78 (1 H, m, ClCH=), and 7.0—7.3 (5 H, m, ArH); δ_C (90 MHz; $CDCl_3$) 112.22 (d, ClCH=, *E*- or *Z*-isomer), 112.74 (d, ClCH=, *E*- or *Z*-isomer); *m/z* 180, 182 (M^+, 2.4, 0.8%), 91 (100), 39 (23), 65 (21), 145 (16), 51 (10), 53 (10), 144 (6), and 77 (5). Isolation of compounds (**10a**) (0.23 g, 1.4 mmol, 14%) and (**11a**) (0.16 g, 1 mmol, 10%) was achieved by liquid chromatography using dichloromethane—cyclohexane (4:1) as the eluant. Their physical and spectroscopic data compared well with those reported [(**10a**);[28,29] (**11a**)[29]].

Reduction of the carbinol (**7b**). According to the general procedure compound (**7b**) (2.89 g, 13.3 mmol) was treated with a 1.0M-$CrCl_2$ solution (53 ml, 53 mmol). Compounds (**9b**) (0.2 g, 1.5 mmol, 11%), (**8b**) (1.38 g, 8.4 mmol, 63%), and (**10b**) (0.26 g, 2.3 mmol, 17%) were isolated by liquid chromatography on silica gel using dichloromethane as the eluant. The physical and spectroscopic data of the products compared well with literature values [(**8b**);[30,31] (**9b**)[32]].

Reduction of the carbinol (**7c**). According to the general procedure compound (**7c**) (10 g, 49 mmol) was treated with a 2.55M-$CrCl_2$ solution (77 ml, 196 mmol). Compounds (**9c**) (1.31 g, 11.3 mmol, 23%), (**8c**) (2.94 g, 19.6 mmol, 40%), and (**10c**) (1.25 g, 12.8 mmol, 26%) were isolated by liquid chromatography on silica gel using dichloromethane–cyclohexane (1:1) as the eluant. The physical and spectroscopic data of the products compared well with literature values [(**8c**);[33,31] (**9c**)[34]].

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