Preparation of Various 1,1-Dihalo-2-haloalkylcyclopropanes and 1,1,2-Trihalocyclopropanes and their Reduction to Dihalides using Tributyltin Hydride

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The title compounds, most of which were obtained by dihalocarbene addition to the corresponding alkenes, are generally reduced to dihalides in good yields. 1,1-Dichloro-2-chloromethyl-2-methylcyclopropane and all the tribromides investigated are attacked regioselectively at the *gem*-dihalo moiety, yielding isomeric mixtures of 1-halo-2-haloalkylcyclopropanes. Trihalides containing both bromo and chloro substituents are always attacked at the C–Br bond; as a consequence substituted 2-bromomethyl-1,1-dichlorocyclopropanes undergo ring opening and form 4,4-dichloro-1-butene derivatives.

gem-Dibromocyclopropanes are usually converted into the corresponding monobromides in good yields when treated with tributyltin hydride (BTH).[1–7] The reaction is completely regiospecific when acyl, alkenyl, alkoxycarbonyl, and hydroxyalkyl groups are attached to the *gem*-dibromocyclopropane,[8,9] and specific attack of the dibromo moiety has also been observed in a few reductions involving 2-alkyl-1,1-dibromo-2-chlorocyclopropanes.[10–12] Whether BTH reduction of *gem*-dibromocyclopropanes with a haloalkyl group attached to the ring in general exhibits the same regiospecificity is, however, not known, but if that is the case, BTH will be a useful reagent for the preparation of specific 1-bromo-2-haloalkylcyclopropanes, which are expected to be convenient starting materials for the synthesis of conjugated dienes.[13,14] We therefore decided to examine the regiochemical and sterochemical aspects of the BTH reduction of selected *gem*-dihalocyclopropanes (halo = chloro, bromo) with a haloalkyl substituent attached to the ring; the results of this investigation are reported here.

Results and discussion

Preparation of trihalides. Most of the *gem*-dihalocyclopropanes (**1**) were prepared by addition of dihalocarbene to the corresponding alkenes under phase-transfer conditions using triethylbenzylammonium chloride (TEBA) as the catalyst. The yield of **1** varied considerably, from 25 % in the case of 1,1-dibromo-2-bromomethylcyclopropane (**1b**) to 69 % in the case of 1,1-dibromo-2-chloro-2-methylcyclopropane (**1g**) (Table 1). When allylic halides were used as the starting materials *gem*-dihalocyclopropanes were obtained in rather low yield due to formation of by-products which conceivably result from initial replacement of halide with trihalomethanide.[15] For trihalides **1d–1h**, on the other hand, the yield is to a much larger extent determined by electronic effects; this is not surprising since there is ample evidence to support the idea that the reactivity of an alkene toward dihalocarbene decreases, although in a rather unsystematic manner, if a halogen atom replaces a hydrogen atom or an alkyl group attached to the double bond.[16–18]

Finally, the course of some of the reactions was influen-

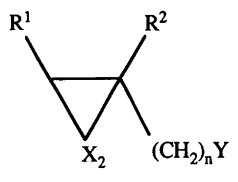

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Table 1. Yields of *gem*-dihalocyclopropanes (**1**), formed by dihalocarbene addition to the corresponding alkenes under phase-transfer conditions.

Compound	R^1	R^2	*n*	X	Y	Yield[a](%)
1a	H	H	1	Br	Cl	26
1b	H	H	1	Br	Br	25
1c	H	H	2	Br	Br	34
1d	CH_3	H	0	Br	Br	21
1e	H	CH_3	0	Cl	Cl	43[b]
1f	H	CH_3	0	Cl	Br	44[b]
1g	H	CH_3	0	Br	Cl	69[b]
1h	H	CH_3	0	Br	Br	52[b]
1i	H	CH_3	1	Cl	Cl	42
1j	H	CH_3	1	Cl	Br	39
1k	H	CH_3	1	Br	Cl	58

[a]After distillation. [b]Yield obtained in the absence of ethanol.

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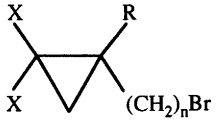
Table 2. The formation of 1,1-diethoxy-2-butyne (**2**) from 1,1,2-tribromo-2-methylcyclopropane (**1h**) under phase-transfer conditions.[a,b]

Molar ratio relative to **1h**			Yield (%)[c]	
NaOH	EtOH	TEBA	**1h**	**2**
3.6	2.6	0.05	38	62
1.5	0	0.05	100	0
3.6	2.6	0	61	39

[a]To simulate the conditions prevailing during the preparation of **1h**, the substrate was used as a 0.7 M solution in dichloromethane. [b]The mixture was stirred at room temperature for 17 h. [c]As a percentage of the crude reaction mixture.

ced by ethanol added to promote cyclopropane generation. It is well established that even small amounts of this alcohol can have a significant effect on the efficiency of *gem*-dihalocyclopropane formation under phase-transfer conditions.[19-21] This was most clearly observed when 1,1,2-tribromo-2-methylcyclopropane (**1h**) was prepared by dibromocarbene addition to 2-bromopropene: when the reaction was performed in the presence of ethanol **1h** was obtained in lower yield than when ethanol was absent. This was in part due to the formation of a new product, *viz.* 1,1-diethoxy-2-butyne (**2**), which was characterized spectroscopically and precipitated as the corresponding 2,4-dinitrophenylhydrazone. When large amounts of ethanol were employed **2** was the major product, indicating that **2** results from an ethanol-sensitive ring opening of **1h**. This was proved to be the case by experiment. In the absence of EtOH **1h** is perfectly stable under phase-transfer conditions (Table 2). Furthermore, it is also evident that when ethanol is added, **2** is formed only somewhat slower without than with TEBA present; consequently, the catalyst is not a prerequisite for the secondary reaction. Investigations are currently under way to uncover the mechanism and the scope of this reaction.

Four trihalides, *viz.* **1l**, **1m**, **1n** and **1o**, were synthesized indirectly by treating the corresponding cyclopropyl alcohols with an excess of phosphorus tribromide. It is noteworthy that **1m** was formed in much higher yield (77 %) than **1l**, **1n** and **1o** (31, 29 and 53 %, respectively). The reason for this reactivity pattern has not been firmly established, but may be related to the fact that the reactions leading to **1l**, **1n** and **1o** take place next to a *gem*-dibromocyclopropyl group.[22]



1l R = Me, n = 1, X = Br
1m R = Me, n = 2, X = Br
1n R = Ph, n = 1, X = Br
1o R = Ph, n = 1, X = Cl

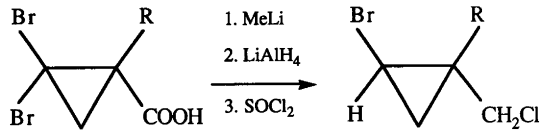
Table 3. Yields and isomeric distribution of dihalides **3** and **4**, obtained by reduction of **1** by tributyltin hydride.

Starting material **1**	Attack at	Product **3**		Product **4**
		cis/trans	Yield (%)[a]	Yield (%)[a]
a	X	45:55	88	
b	X	41:59	66	
c	X	45:55	54	
d	X	33:67	70	
e	–	–	0	
f	Y	–	74	
g	X	38:62	84	
h	X	27:73	77	
i	X	35:65	56	
j	Y			27
k	X	35:65	50	
l	X	36:64	50	
m	X	36:64	73	
n	X	57:43	52	
o	Y			71

[a]Yields obtained by distillation.

A comment regarding the ^{1}H NMR spectra of 1,1-dibromo-2-bromomethyl-2-phenylcyclopropane (**1n**) and 2-bromomethyl-1,1-dichloro-2-phenylcyclopropane (**1o**) is appropriate. If no long-range coupling were present both compounds should give rise to spectra containing two AB systems, one for each of the methylene groups. However, this is not the case; in both spectra obtained at 89.55 MHz the A part of the system consists of two narrow peaks whereas the B part contains two groups of broader lines. This observation indicates that **1n** and **1o** exhibit the same type of unusual long-range coupling that we have previously reported for 1,1-dibromo-2-phenyl-2-(2-propenyl)cyclopropane.[23]

Reduction of trihalides **1**. When reacted with a 5 % molar excess of BTH at room temperature the trihalides were converted into dihalides in good yields in all cases but one (Table 3). The exception is **1e** which is completely unreactive under our reaction conditions (room temperature) because there are three chloro atoms directly attached to the ring. Otherwise the BTH reductions occur with a high degree of selectivity in several respects. Firstly, all trihalides containing both bromo and chloro substituents are always attacked at the C–Br bond irrespective of its position; thus, reduction of 1-bromo-2,2-dichloro-1-methyl-cyclopropane (**1f**) yields 1,1-dichloro-2-methylcyclopropane (**3f**) as the only product and 1-bromo-2-chloro-2-methylcyclopropane (**3g**) is selectively obtained from 1,1-dibromo-2-chloro-2-methylcyclopropane (**1g**) under the same conditions. Secondly, all the tribromides and the only trichloride that turned out to be reactive (**1i**), are attacked regioselectively at the *gem*-dihalo moiety; thus, 1,1,2-tribromo-2-methylcyclopropane (**1h**) gives only 1,2-dibromo-2-methylcyclopropane (**3g**) and **1i** is selectively converted into 1-chloro-2-chloromethyl-2-methylcyclopropane (**3i**). Finally,

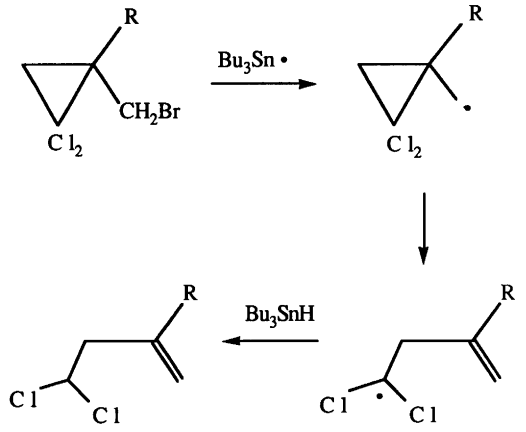


R = H, CH_3

Scheme 1.

all dihalides, except those furnished from **1f**, **1j** and **1o**, are formed as mixtures of two isomers in an approximate ratio of 2:3. On the assumption that electrostatic interactions cause halogen atoms attached to the ring to shift protons *cis* to it to lower field[24] we have reached the conclusion that the *trans* isomer predominates in all cases. This conclusion is supported by the independent synthesis of *trans*-**3a** and *trans*-**3k** (Scheme 1) which turned out to be identical with the predominant isomer of **3a** and **3k**, respectively.

The course of reaction changed completely when 2-bromomethyl-1,1-dichloro-2-methylcyclopropane (**1j**) and 2-bromomethyl-1,1-dichloro-2-phenylcyclopropane (**1o**) were treated with BTH. In both cases no cyclopropane was detected but rather an alkene; 4,4-dichloro-2-methyl-1-butene (**4j**) was obtained in 27 % yield from **1j**, and **1o** afforded 4,4-dichloro-2-phenyl-1-butene (**4o**) which was isolated in 71 % yield. The formation of these ring-opened products can be rationalized as depicted in Scheme 2. In



Scheme 2.

accordance with the general reaction pattern summarized above the bromo substituent is specifically attacked, generating a radical next to the ring. This intermediate is apparently unstable like the cyclopropylmethyl radical[25,26] and rearranges to the 3-butenyl radical which is trapped by BTH and gives **4**. Experiments are under way to examine the synthetic potential of this reaction.

Experimental

General. IR spectra were recorded on a Shimadzu IR-435 spectrophotometer with the compounds as liquid films unless stated otherwise. ^{1}H NMR spectra were obtained on Jeol PMX 60 SI (60 MHz) and Jeol FX 90Q (89.55 MHz) spectrometers and ^{13}C NMR spectra on a Jeol FX 90Q (22.50 MHz) instrument. $DCCl_3$ was used as the solvent unless stated otherwise and tetramethylsilane (TMS) was added as an internal reference. Chemical shifts are reported in ppm downfield from TMS. GLC analyses were performed either on a Carlo Erba HRGC 5300 Mega Series gas chromatograph equipped with FID and a Chrompack CP-Sil 5CB fused silica column (26 m×0.32 mm i.d.) and connected to an LDC/Milton Roy CI-10B integrator or on a Varian 3700 gas chromatograph which was equipped with a TCD and a Carbowax 20M or an OV-17 column and attached to a Varian 9176 recorder. No corrections were made for response ratios. Mass spectra were obtained on a VG 7070H Micromass spectrometer operated in the EI mode at 70 eV. The spectra are reported as *m/z* (% rel. int.).

Preparation of gem*-dihalocyclopropanes.* Most of the compounds were synthesized from the corresponding alkene on a 20 mmol scale under phase-transfer conditions in the presence of some ethanol as described in the literature.[20,27] The yields are summarized in Table 1.

1,1-Dibromo-2-chloromethylcyclopropane (**1a**),[28] from 3-chloropropene, b.p. 84–86 °C/11 mmHg (lit.[28] b.p. 95–99 °C/22 mmHg).

1,1-Dibromo-2-bromomethylcyclopropane (**1b**),[29,30] from 3-bromopropene, b.p. 78 °C/7.5 mmHg (lit.[29] 102–104 °C/17 mmHg).

1,1-Dibromo-2-(2-bromoethyl)cyclopropane (**1c**), from 4-bromo-1-butene, b.p. 47 °C/0.15 mmHg. IR: 1445 (m), 1435 (m), 1425 (m), 1261 (m), 1043 (m), 680 (s) cm^{-1}; ^{1}H NMR (89.55 MHz): δ 1.17–2.27 (5 H, m), 3.54 (2 H, t *J* 7 Hz); MS: 310 (1, M^+), 308 (3, M^+), 306 (3, M^+), 304 (1, M^+), 282 (2), 280 (6), 278 (6), 276 (2), 201 (17), 199 (35), 197 (18), 145 (50), 65 (70). Mol. wt. of **1c**: Calc. for $C_5H_7{}^{81}Br_2{}^{79}Br$ 307.8057. Found 307.8068.

trans*-1,1,2-Tribromo-3-methylcyclopropane* (**1d**), from (*E*)-1-bromopropene contaminated with (*Z*)-1-bromopropene, b.p. 86 °C/8.5 mmHg. IR: 3050 (m), 1445 (m), 1380 (s), 1240 (s), 1140 (m), 1120 (m), 1035 (m), 1010 (m), 870 (s), 800 (s), 730 (s), 655 (s) cm^{-1}; ^{1}H NMR (60 MHz, CCl_4): δ 1.29 (3 H, d, *J* 6 Hz), 1.50–2.13 (1 H, m), 3.72 (1 H, d, *J* 9 Hz); MS: 296 (< 1, M^+), 294 (1, M^+), 292 (1, M^+), 290 (<

1, M^+), 215 (48), 213 (100), 211 (51), 175 (4), 173 (8), 171 (5), 133 (54), 131 (57), 51 (75). Mol. wt. of **1d**: Calc. for $C_4H_5{}^{79}Br_3$ 289.7941. Found 289.7955.

1,1,2-Trichloro-2-methylcyclopropane (**1e**), from 2-chloropropene, b.p. 85–86 °C/17 mmHg. IR: 3080 (m), 1445 (s), 1415 (s), 1382 (s), 1165 (s), 1085 (s), 1065 (s), 1030 (s), 765 (s) cm^{-1}; ^1H NMR (60 MHz, CCl_4): δ 1.66 (1 H, d, *J* 8.5 Hz), 1.79 (1 H, d, *J* 8.5 Hz), 1.87 (3 H, s); MS: 160 (1, M^+), 147 (1), 145 (7), 143 (10), 127 (9), 125 (62), 123 (100), 87 (83), 51 (70). Anal. $C_4H_5Cl_3$: C, H.

1-Bromo-2,2-dichloro-1-methylcyclopropane (**1f**), from 2-bromopropene, b.p. 45–46 °C/16 mmHg. IR: 3080 (w), 1438 (s), 1420 (s), 1150 (s), 1055 (s), 1025 (s), 870 (m), 755 (s) cm^{-1}; ^1H NMR (60 MHz, CCl_4): δ 1.78 (2 H, br s), 2.08 (3 H, s); MS: 193 (0.4), 191 (0.6), 189 (1.4), 171 (2), 169 (9), 167 (7), 133 (6), 131 (7), 127 (13), 126 (3), 125 (72), 124 (6), 123 (100), 111 (4), 109 (9), 95 (13), 89 (39), 88 (10), 87 (100). Anal. $C_4H_5BrCl_2$: C, H.

1,1-Dibromo-2-chloro-2-methylcyclopropane (**1g**), from 2-chloropropene, b.p. 69–70 °C/7.6 mmHg (lit.[12] b.p. 35–38 °C/0.6 mmHg).

1,1,2-Tribromo-2-methylcyclopropane (**1h**), from 2-bromopropene, b.p. 89–90 °C/14 mmHg. IR: 3080 (w), 1438 (s), 1418 (s), 1145 (s), 1083 (m), 1057 (s), 1010 (s), 855 (w), 818 (m), 690 (s) cm^{-1}; ^1H NMR (60 MHz, CCl_4): δ 1.84 (1 H, d, *J* 8.5 Hz), 1.96 (1 H, d, *J* 8.5 Hz), 2.10 (3 H, s); MS: 215 (48), 213 (100), 211 (52), 175 (20), 173 (35), 171 (20), 133 (75), 131 (75), 51 (85). Anal. $C_4H_5Br_3$: C, H.

When **1h** was prepared in the presence of ethanol 1,1-diethoxy-2-butyne (**2**) was formed as a by-product. This compound was isolated by column chromatography (SiO_2, $CHCl_3$) and precipated as the 2,4-dinitrophenylhydrazone derivative (**2**-2,4-DNP). **2**: IR: 2185 (m), 1675 (m), 1250 (m), 1140 (s), 1070–1030 (s, broad), 990 (s), 900 (m), 725 (m) cm^{-1}; ^1H NMR (89.55 MHz): δ 1.22 (6 H, t, *J* 7.1 Hz), 1.87 (3 H, d, *J* 2 Hz), 3.38–3.91 (4 H, m), 5.21 (1 H, d, *J* 2 Hz); ^{13}C NMR: δ 3.4 (CH_3), 15.1 (CH_3), 60.7 (CH_2), 75.3 (C), 81.9 (C), 91.7 (CH); MS: 141 (2), 113 (2), 98 (6), 97 (100), 85 (5), 70 (4), 69 (85). **2**-2,4-DNP: m.p. 140.5–141 °C (lit.[31] m.p. 142.5 °C); ^1H NMR (60 MHz, CCl_4): δ 2.21 (3 H, d, *J* 2 Hz), 6.67 (1 H, d, *J* 2 Hz), 7.20 (1 H, s), 7.85 (1 H, d, *J* 9 Hz), 8.28 (1 H, dd, *J* 3 and 9 Hz), 9.07 (1 H, d, *J* 3 Hz).

1,1-Dichloro-2-chloromethyl-2-methylcyclopropane (**1i**), from 3-chloro-2-methylpropene, b.p. 84 °C/29 mmHg (lit.[22] b.p. 86 °C/30 mmHg).

2-Bromomethyl-1,1-dichloro-2-methylcyclopropane (**1j**), from 3-bromo-2-methylpropene (17.66 g, 0.24 mol) and chloroform (39 ml, 0.48 mol), b.p. 72–74 °C/10.5 mmHg. IR: 1450 (s), 1435 (s), 1425 (s), 1385 (s), 1325 (m), 1275 (m), 1230 (s), 1150 (m), 1080 (s), 1040 (s), 960 (s), 905 (m), 855 (m), 765 (s), 640 (m) cm^{-1}; ^1H NMR (89.55 MHz): δ 1.47 (2 H, s), 1.53 (3 H, s), 3.52 (1 H, d, *J* 10.5 Hz), 3.67 (1 H, d, *J* 10.5 Hz); ^{13}C NMR: δ 19.9 (CH_3), 31.4 (C), 33.6 (CH_2), 39.4 (CH_2), 67.2 (C); MS: 218 (3), 216 (2), 169 (12), 167 (10), 139 (44), 138 (17), 137 (80), 136 (20), 125 (61), 123 (100), 109 (21), 103 (26).

1,1-Dibromo-2-chloromethyl-2-methylcyclopropane (**1k**),[15] from 3-chloro-2-methylpropene, b.p. 86 °C/9 mmHg. IR: 1455 (m), 1425 (m), 1265 (s), 1080 (m), 1060 (m), 1040 (m), 1025 (m), 725 (s), 680 (s) cm^{-1}; ^1H NMR (89.55 MHz): δ 1.55 (3 H, s), 1.64 (2 H, m), 3.67 (1 H, d, *J* 11.5 Hz), 3.78 (1 H, d, *J* 11.5 Hz).

1,1-Dibromo-2-bromomethyl-2-methylcyclopropane (**1l**). A solution of 2,2-dibromo-1-methylcyclopropylmethanol[32,33] (1.30 g, 5.33 mmol) and phosphorus tribromide (0.68 g, 2.51 mmol) in tetrachloromethane (10 ml) was stirred for 0.5 h. The mixture was then hydrolyzed and extracted with tetrachloromethane. The combined extracts were dried with anhydrous calcium chloride. Filtration and evaporation of the solvent left 0.50 g (31 %) of a slightly yellow liquid which was almost pure **1l**.[15] IR: 1448 (s), 1425 (s), 1265 (s), 1223 (s), 1073 (s), 1042 (s), 1020 (s), 700 (s), 650 (s) cm^{-1}.

1,1-Dibromo-2-(2-bromoethyl)-2-methylcyclopropane (**1m**). A mixture of 2-(2,2-dibromo-1-methylcyclopropyl) ethanol[34] (15.0 g, 58.1 mmol) and phosphorus tribromide (5.2 g, 19.2 mmol) was stirred at 20 °C for 0.5 h. The reaction mixture was then hydrolyzed and extracted with tetrachloromethane and the combined extracts were dried with anhydrous calcium chloride. Usual work-up gave a residue which upon distillation yielded 14.3 g (77 %) of **1m**, b.p. 88–89 °C/1.2 mmHg. IR: 1448 (m), 1415 (m), 1210 (m), 1040 (m), 1020 (m), 782 (s), 759 (s), 685 (m) cm^{-1}; ^1H NMR (60 MHz, CCl_3): δ 1.42 (3 H, s), 1.47 (1 H, d, *J* 7 Hz), 1.57 (1 H, d, *J* 7 Hz), 2.20 (2 H, t, *J* 8.5 Hz), 3.48 and 3.51 (2 H, 2 t, *J* 8.5 Hz); MS: 324 (1, M^+), 322 (3, M^+), 320 (3, M^+), 318 (1, M^+), 243 (7), 241 (15), 239 (8), 215 (48), 213 (100), 211 (52), 161 (23), 159 (21), 121 (20), 119 (52), 117 (47), 55 (83). Mol. wt. of **1m**: Calc. for $C_9H_9{}^{81}Br^{79}Br_2$ 319.8234. Found 319.8280.

1,1-Dibromo-2-bromomethyl-2-phenylcyclopropane (**1n**) was prepared from 2,2-dibromo-1-phenylcyclopropylmethanol[33] (39.4 g, 0.13 mol) using phosphorus tribromide (78.1 g, 0.29 mol) as described in the literature.[35] The product, 13.7 g (29 %), was obtained pure after column chromatography (SiO_2, 5 % $CHCl_3$ in hexane), m.p. 67–68 °C. IR (CCl_4): 3080 (sh), 3063 (m), 3035 (m), 1603 (m), 1580 (w), 1495 (s), 1448 (s), 1441 (s), 1428 (s), 1225 (s), 1025 (s), 978 (w), 901 (w), 695 (s), 665 (s), 565 (s) cm^{-1}; ^1H NMR (89.55 MHz): δ 2.00 (1 H, d, *J* 8.1 Hz), 2.25 (1 H, m), 3.84 (1 H, d, *J* 10.4 Hz), 3.96 (1 H, m), 7.36 (5 H, br s); ^{13}C NMR: δ 34.8, 40.1, 42.4, 128.2, 128.3, 129.8, 138.3; MS: 289 (3), 286 (7), 208 (4), 207 (22), 206 (6), 205 (22), 204 (3), 191 (3),

128 (23), 127 (100), 126 (14), 125 (4), 114 (9), 102 (24), 101 (12), 77 (20), 64 (16), 63 (13), 51 (26), 50 (12). Anal. $C_{10}H_9Br_3$: C, H.

2-Bromomethyl-1,1-dichloro-2-phenylcyclopropane (**1o**) was prepared from 2,2-dichloro-1-phenylcyclopropylmethanol which was obtained in 36% yield, after hydrolytic work-up and column chromatography (SiO_2, $CHCl_3$), by LAH reduction[33] of ethyl 2,2-dichloro-1-phenylcyclopropanecarboxylate.[36] Data for the alcohol: IR (CCl_4): 3580 (s), 3450 (m), 3060 (m), 3035 (m), 1603 (m), 1498 (s), 1425 (s), 1385 (s), 1110 (s), 1045 (s), 1013 (s), 908 (s), 695 (m) cm^{-1}; ^1H NMR (89.55 MHz): δ 1.70–1.90 (2 H, m), 2.25 (1 H, s), 3.67–3.98 (2 H, m), 7.30 (5 H, br s); ^{13}C NMR: δ 30.0, 41.7, 64.0, 68.3, 127.8, 128.4, 129.7, 137.3; MS: 189 (2), 168 (10), 166 (31), 158 (5), 157 (15), 154 (53), 142 (3), 132 (3), 131 (11), 128 (8), 122 (95), 119 (13), 118 (9), 117 (49), 107 (9), 105 (15), 94 (12), 93 (100), 91 (12), 66 (13), 64 (16). Anal. $C_{10}H_{10}Cl_2O$: C, H.

When 2,2-dichloro-1-phenylcyclopropylmethanol (15.20 g, 7 mmol) was treated with phosphorus tribromide (54.14 g, 0.20 mol) as described in the literature,[35] pure **1o** (10.43 g, 53%) was obtained by column chromatography (SiO_2, $CHCl_3$), m.p. 55–58 °C. IR (CCl_4): 3060 (m), 3030 (m), 1604 (m), 1498 (s), 1450 (s), 1438 (s), 1425 (s), 1255 (s), 1230 (s), 1150 (s), 1110 (s), 1044 (s), 981 (m), 884 (m), 700 (m), 583 (s) cm^{-1}; ^1H NMR (89.55 MHz): δ 1.83 (1 H, d, *J* 7.6 Hz), 2.07 (1 H, m), 3.80 (1 H, d, *J* 10.5 Hz), 3.87 (1 H, m), 7.36 (5 H, m); ^{13}C NMR: δ 33.2, 40.4, 41.2, 66.4, 128.2, 128.4, 129.8, 137.1; MS: 200 (4), 199 (3), 198 (23), 197 (5), 196 (35), 183 (8), 164 (4), 163 (33), 162 (13), 161 (100), 160 (5), 149 (8), 147 (24), 127 (17), 126 (61), 125 (33), 113 (15), 102 (85), 101 (22), 76 (40), 75 (10), 74 (10), 62 (21). Anal. $C_{10}H_9BrCl_2$: C, H.

Reduction of trihalides with tributylin hydride (BTH). The reductions of **1** were generally carried out on a 5–20 mmol scale as described in the literature.[9] Some reactions were carried out without solvent. BTH was prepared as described in the literature.[37] The following dihalides were obtained; their yields and isomer distributions are compiled in Table 3.

1-Bromo-2-chloromethylcyclopropane (**3a**), b.p. 46–47 °C/13 mmHg. IR: 3050 (w), 1438 (m), 1370 (m), 1252 (s), 1035 (m), 818 (w), 708 (m) cm^{-1}; ^1H NMR (60 MHz): δ 0.7–2.0 (3 H, m), 2.6–3.9 (3 H, m); ^{13}C NMR: δ (major isomer) 15.8 (CH_2), 19.0 (CH), 24.4 (CH), 46.3 (CH_2Cl); δ (minor isomer) 16.3 (CH_2), 17.7 (CH), 21.7 (CH), 45.9 (CH_2Cl). Anal. C_4H_6BrCl: C, H. The less abundant isomer had the shorter retention time on an OV-17 GLC column.

1-Bromo-2-bromomethylcyclopropane (**3b**), b.p. 37 °C/0.04 mmHg. IR: 1435 (m), 1370 (m), 1265 (m), 1220 (s), 1035 (m), 685 (m) cm^{-1}; ^1H NMR (60 MHz, CCl_4): δ 0.6–2.2 (3 H, m), 2.6–3.6 (3 H, m); MS: 216 (2, M^+), 214 (5, M^+), 212 (2, M^+). Mol. wt. of **2b**: Calc. for $C_4H_6{}^{79}Br_2$ 211.8836. Found 211.8844. The minor isomer had the shorter retention time on an OV-17 GLC column.

1-Bromo-2-(2-bromoethyl)cyclopropane (**3c**), b.p. 30 °C/2.7 mmHg. IR: 1435 (m), 1425 (m), 1260 (s), 1215 (m), 815 (m), 680 (w) cm^{-1}; ^1H NMR (60 MHz, CCl_4): δ 0.5–1.5 (3 H, m), 1.7–2.3 (2 H, m), 2.50–2.73 and 2.89–3.22 (1 H, 2 m in the ratio 45:55), 3.30–3.70 (2 H, m); MS: 230 (2, M^+), 228 (4, M^+), 226 (2, M^+). Mol. wt. of **3c**: Calc. for $C_5H_8{}^{79}Br_2$ 225.8993. Found 225.9012. The less abundant isomer had shorter retention time on a Carbowax 20M GLC column.

1,2-Dibromo-3t-methylcyclopropane (**3d**), b.p. 46–48 °C/46 mmHg. IR: 1260 (m), 1238 (m), 1205 (m), 1010 (m), 645 (m) cm^{-1}; ^1H NMR (60 MHz, CCl_4): δ 0.9–1.5 (4 H, m), 2.75 and 3.20–3.38 (1 H, d, *J* 5 Hz and m, respectively, in the ratio 33:67). The minor isomer had the shorter retention time on an OV-17 GLC column.

1,1-Dichloro-2-methylcyclopropane (**3f**), b.p. 32 °C/80 mmHg. The reaction was carried out without any solvent. IR: 3020 (w), 1448 (m), 1428 (s), 1223 (m), 1120 (s), 1081 (s), 1039 (s), 892 (m), 860 (w), 740 (s) cm^{-1}; ^1H NMR (60 MHz): δ 0.7–1.8 (complex m); ^{13}C NMR: δ 14.8 (CH_3), 25.4 (CH), 27.6 (CH_2), 61.7 (C). Anal. $C_4H_6Cl_2$: C, H.

1-Bromo-2-chloro-2-methylcyclopropane (**3g**), b.p. 58 °C/25 mmHg (lit.[12] b.p. 100–103 °C). IR: 1440 (w), 1380 (w), 1158 (w), 1148 (w), 1015 (m), 785 (s), 760 (s), 695 (m) cm^{-1}. The less abundant isomer had the longer retention time on an OV-17 GLC column.

1,2-Dibromo-1-methylcyclopropane (**3h**). The reaction was carried out without solvent. IR: 3050 (w), 1420 (m), 1380 (m), 1235 (m), 1140 (s), 1035 (m), 900 (w), 785 (s) cm^{-1}. Anal. $C_4H_6Br_2$: C, H. The isomers were seperated by distillation; the *trans* isomer: b.p. 38 °C/8.0 mmHg; ^1H NMR (89.55 MHz): δ 0.9–2.0 (2 H, m, AB part of an ABX system), 1.91 (3 H, s), 3.50 (1 H, dd, X part of an ABX system, *J* 5.6 and 8.8 Hz); the *cis* isomer: b.p. 72 °C/10.5 mmHg; ^1H NMR (89.55 MHz): δ 1.2–1.6 (2 H, m, AB part of an ABX system), 1.83 (3 H, s), 2.84 (1 H, m, X part of an ABX system, *J* 5.7 and 8.4 Hz).

1-Chloro-2-chloromethyl-2-methylcyclopropane (**3i**), b.p. 46–48 °C/7 mmHg. IR: 3080 (w), 1445 (s), 1430 (s), 1270 (s), 1035 (s), 950 (m), 765 (s), 720 (s) cm^{-1}; ^1H NMR (60 MHz, CCl_4): δ 0.63–1.20 (2 H, m), 1.25 and 1.4 (3 H, 2 s in an approximate ratio of 2:3), 2.90–3.12 (1 H, m), 3.33 and 3.61 (2 H, 2 br s in an approximate ratio of 3:2). Anal. $C_5H_8Cl_2$: C, H. The less abundant isomer had the shorter retention time on an OV-17 GLC column.

BTH reduction of 2-bromomethyl-1,1-dichloro-2-methylcyclopropane (**1j**) (4.36 g, 20 mmol) according to the general procedure afforded 0.72 g (27%) of 4,4-dichloro-2-

methyl-1-butene (**4j**), b.p. 46–48 °C/31 mmHg. IR: 3060 (m), 1715 (m), 1650 (m), 1440 (s), 1375 (m), 1325 (w), 1265 (s), 1220 (m), 1010 (m), 930 (s), 900 (s), 755 (s), 695 (s), 650 (s) cm^{-1}; ^1H NMR (60 MHz): δ 1.78 (3 H, br s), 2.88 (2 H, d, *J* 6 Hz), 4.75 (2 H, m), 5.77 (1 H, t, *J* 6 Hz); ^{13}C NMR: δ 22.1 (CH_3), 51.8 (CH_2), 71.2 (CH), 115.7 (CH_2), 139.3 (C); MS: 140 (17), 138 (26), 123 (4), 105 (11), 103 (34), 102 (23), 90 (86), 89 (100), 87 (12). Anal. $C_5H_8Cl_2$: C, H.

1-Bromo-2-chloromethyl-2-methylcyclopropane (**3k**), b.p. 62–64 °C/11 mmHg. IR: 3050 (w), 1450 (s), 1430 (m), 1380 (m), 1300 (s), 1265 (s), 1215 (s), 1080 (m), 1035 (m), 955 (w), 720 (s), 600 (s) cm^{-1}; ^1H NMR (60 MHz, CCl_4): δ 0.70–1.60 (2 H, m), 1.28 and 1.40 (3 H, 2 s in a ratio of 35:65), 2.80–3.07 (1 H, m), 3.36 and 3.65 (2 H, 2 s in a ratio of 65:35); MS: 182 (0.1, M^+), 149 (2), 147 (2), 135 (42), 133 (60), 105 (24), 103 (69), 67 (78), 41 (100). Mol. wt. of **3k**: Calc. for $C_5H_8{}^{79}Br^{35}Cl$ 181.9498. Found 181.9504. The minor isomer had the shorter retention time on an OV-17 GLC column.

1-Bromo-2-bromomethyl-2-methylcyclopropane (**3l**), b.p. 48–50 °C/2.3 mmHg. IR: 3070 (w), 1450 (s), 1430 (s), 1380 (m), 1300 (s), 1265 (m), 1220 (s), 1035 (s), 955 (m), 720 (m), 710 (s) cm^{-1}; ^1H NMR (60 MHz, CCl_4): δ 0.7–1.6 (2 H, m), 1.30 and 1.42 (3 H, 2 s in the ratio 36:64), 2.78–3.50 (1 H, m), 3.38 and 3.65 (2 H, 2 s, the one at higher field is the stronger). Anal. $C_5H_8Br_2$: C, H. The minor isomer had the shorter retention time on an OV-17 GLC column.

1-Bromo-2-(2-bromoethyl)-2-methylcyclopropane (**3m**), b.p. 55–60 °C/7 mmHg. IR: 3060 (w), 1450 (m), 1430 (m), 1375 (w), 1270 (m), 1205 (m), 1025 (m), 795 (m), 755 (m), 650 (m) cm^{-1}; ^1H NMR (60 MHz): δ 0.5–1.5 (2 H, m), 1.56 and 1.60 (3 H, 2 s in a 2:3 ratio); MS: 244 (2), 242 (3), 240 (2), 164 (6), 163 (23), 162 (7), 161 (24), 160 (3), 135 (22), 133 (22), 121 (7), 191 (8), 109 (3), 107 (4), 93 (2), 83 (3), 82 (10), 81 (100).

1-Bromo-2-bromomethyl-2-phenylcyclopropane (**3n**). Reduction of **1n** (3.19 g, 8.6 mmol) gave after column chromatography (SiO_2, pentane) 1.50 g (52 %) of **3n**. IR (CCl_4): 3060 (s), 3030 (s), 1605 (m), 1500 (s), 1495 (s), 1445 (s), 1290 (s), 1220 (s), 1025 (s), 902 (m), 695 (m) cm^{-1}; ^1H NMR (89.55 MHz): δ (major isomer) 1.26–1.88 (2 H, m), 3.45 (1 H, dd, *J* 7.8 and 5.2 Hz), 3.72–3.99 (2 H, m), 7.37 (5 H, br s); δ (minor isomer) 1.54–1.74 (2 H, m), 3.32 (1 H, d, *J* 10.4 Hz), 3.32 (1 H, dd, *J* 7.6 and 5.1 Hz), 3.76–3.89 (1 H, m), 7.33 (5 H, br s). The major isomer had the shorter retention time on an OV-17 GLC column.

BTH reduction of 2-bromomethyl-1,1-dichloro-2-phenylcyclopropane (**1o**) (5.6 g, 20 mmol) gave 2.9 g (71 %) of 4,4-dichloro-2-phenyl-1-butene (**4o**), b.p. 72–73 °C/0.3 mmHg. IR: 1630 (m), 1600 (w), 1575 (w), 1495 (s), 1445 (m), 1428 (m), 1265 (s), 1220 (m), 943 (s), 908 (s), 785 (s), 700 (s), 665 (s) cm^{-1}; ^1H NMR (89.55 MHz): δ 3.39 (2 H, dd, *J* 6.7 and <1.0 Hz), 5.24 (1 H, m), 5.43 (1 H, br s), 5.64 (1 H, t, *J* 6.7 Hz), 7.30 (5 H, br s); ^{13}C NMR: δ 50.0 (CH_2), 71.2 (CH), 177.5 (CH_2), 126.3 (CH), 128.1 (CH), 128.7 (CH), 139.3 (C), 142.9 (C). MS: 202 (10), 200 (17), 165 (9), 151 (30), 130 (12), 129 (100), 128 (21), 127 (10), 116 (11), 115 (52), 103 (23), 102 (13). Anal. $C_{10}H_{10}Cl_2$: C, H.

Preparation of trans-*1-bromo-2-chloromethylcyclopropane* (trans-**3a**). Ruthenium tetraoxide oxidation of 1,1-dibromo-2-phenylcyclopropane (5.52 g, 20 mmol) as described in the literature[38,39] gave 1.5 g (30 %) of 2,2-dibromocyclopropanecarboxylic acid. Treatment of this acid with methyllithium at 0 °C gave *trans*-2-bromocyclopropanecarboxylic acid (1.0 g, 100 %).[34] This acid was reduced at room temperature using a suspension of lithium aluminium hydride (0.30 g, 8 mmol) in dry diethyl ether (20 ml). Usual work-up (hydrolysis with 10 % hydrochloric acid, extraction with diethyl ether) gave crude *trans*-2-bromocyclopropylmethanol which was treated directly with triethylamine (0.62 g, 6.2 mmol) and thionyl chloride (0.90 ml, 1.48 g, 12.4 mmol) at 70 °C for 1 h to give *trans*-1-bromo-2-chloromethylcyclopropane (0.95 g crude product, 95 % pure according to GLC analysis) after hydrolysis (10 % hydrochloride acid) and subsequent diethyl ether extraction.

Preparation of trans-*1-bromo-2-chloromethyl-2-methylcyclopropane* (trans-**3k**). Reduction of *trans*-2-bromo-1-methylcyclopropanecarboxylic acid[34] (3.25 g, 18.2 mmol) with lithium aluminium hydride (0.69 g, 18.2 mmol) in dry diethyl ether (150 ml) at 0 °C (1 h) and at room temperature (2 h) gave after hydrolytic work-up and distillation 2.0 g (67 %) of *trans*-2-bromo-1-methylcyclopropylmethanol, b.p. 96–98 °C/17 mmHg (lit.[6] b.p. 87–88 °C/17 mmHg for a *cis/trans* mixture), which (0.40 g, 2.5 mmol) upon treatment with thionyl chloride (0.66 g, 5.5 mmol) in the presence of triethylamine (0.27 g, 2.7 mmol) at 70 °C afforded *trans*-1-bromo-2-chloromethyl-2-methylcyclopropane (0.32 g crude product, 90 % pure according to GLC analysis) after hydrolysis (10 % hydrochloric acid) and extraction (diethyl ether).

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