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Bromine–magnesium exchange in *gem*-dibromocyclopropanes using Grignard reagents

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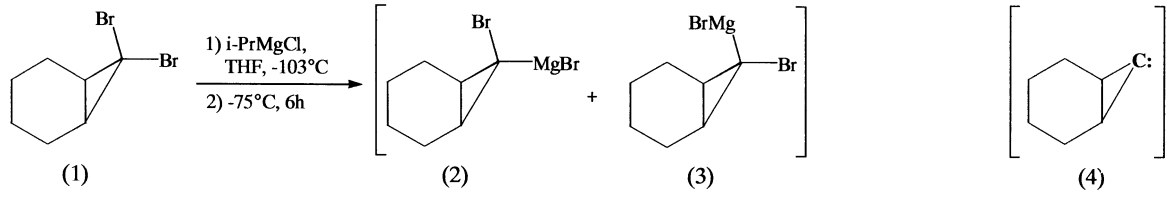
Abstract—Reaction of *gem*-dibromocyclopropanes with ethylmagnesium bromide at ambient temperature leads to very high yields of allenes; when cyclopropylidene–allene ring opening is suppressed, alternative carbenic products are observed, although other reactions compete. When the reactions are carried out at −60°C, a 1-bromo-1-(bromomagnesio)-cyclopropane is formed which may be trapped by a number of electrophiles.

It has been known for nearly 40 years that the reaction of a *gem*-dibromocyclopropane with an alkyllithium, normally methyllithium, leads in many cases to very high yields of an allene, apparently derived through lithium–bromine exchange and then loss of lithium bromide to give a cyclopropylidene or a related carbenoid.[1] The lithiobromocyclopropane can be intercepted by reaction with an electrophile, although in many cases this can only be observed at low temperature, often below −100°C. The rearrangement of the cyclopropylidene to allene can also be suppressed when the latter is strained or when a favourable alternative carbene reaction is available.[2] The reaction of *gem*-dibromocyclopropanes with metallic sodium, lithium or magnesium (a reaction predating the use of an alkyllithium)[3,4] or the reaction of *gem*-dichlorocyclopropanes with magnesium in the presence of ethyl bromide[5] has also been reported to lead to allenes, although in general yields are only moderate. The reaction of such dibromides with methylmagnesium bromide in ether has been reported to follow a quite different course, leading to the formation of a monobromocyclopropane at ambient temperature in a relatively slow reaction;[6] we have recently reported that, with a number of Grignard reagents, this hydrodebromination is strongly promoted by titanium isopropoxide.[6] Seyferth and Lambert also reported, however, that the reaction of a *gem*-dibromocyclopropane, 7,7-dibromobicyclo[4.1.0]heptane, with 2-propylmagnesium chloride in tetrahydrofuran (THF) at −103°C and then at −75°C for 6 h leads to organomagnesium species (**2** and **3**) that can be trapped effectively at low temperature by reaction with acid, again giving the monobromides or by trimethyltin chloride, giving a single isomer, *endo*-7-bromo-*exo*-7-trimethylstannylbicyclo[4.1.0]heptane. Apparently, under these conditions, hydrogen abstraction from the solvent does not occur.[7] Reaction of the same dibromide with MeMgBr in THF at ambient temperature is reported by Seyferth and Prokai to lead to an exothermic reaction and also to the formation of the corresponding *exo*- and *endo*-monobromides; in this case, the origin of the hydrogen introduced in the reaction was shown to be the solvent.[8] No products characteristic of the formation of the cyclopropylidene (**4**) were observed (Scheme 1).

We were surprised, therefore, to see the very brief report by



Scheme 1.

Keywords: bromine–magnesium exchange; *gem*-dibromocyclopropanes; Grignard reagent; cyclopropylidenes.
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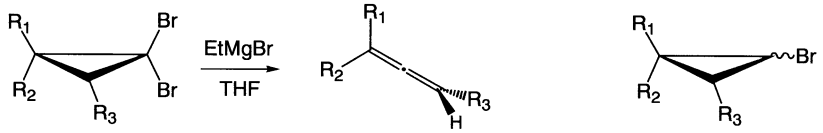


(5) (6) (7)

	R_1	R_2	R_3
(a)	Me	Ph	H
(b)	Ph	Ph	H
(c)	Ph	H	H
(d)	H	$-(CH_2)_6-$	
(e)	H	n-Hexyl	H

Scheme 2.

Table 1. Reaction of *gem*-dibromocyclopropanes with ethylmagnesium bromide in THF at ambient temperature

Starting material	Amount (mmol)	Amount of Grignard (mol equiv.)	Time of addition (min)	Time of stirring (min)	Products (by GLC)			Isolated yield (%)
					5	**6**	**7**	
5a	3	1.3	7	30	14	86	Trace	–
	3	1.5	7	30	3	97	Trace	–
	10	1.7	9	30	–	100	Trace[a]	96
5b	10	1.3	4	30	–	99	–	96
5c	10	1.3	5	30	–	100	–	92
5d	3	2.0	3	30	2	98	–	–
	10	2.0	4	60	–	99	–	93
5e	3	1.7	7	30	2	94	2	–
	10	1.7	12	60	Trace	95	1[b]	91

[a] Less than 0.5% by GLC. If the Grignard reagent was prepared from 98% pure magnesium (rather than 99.98% pure as in all other experiments), 2% (**7a**) was obtained by GLC under the same conditions.
[b] The reactions in this table were carried out using freshly distilled THF. When this experiment was carried out using THF that had been standing far one week without excluding air and light the amount of monobromides (**7e**) was 17% and allene (**6e**) 79%.

Table 2. Reaction of (**5a**) with different Grignard reagents in THF at ambient temperature

Grignard	Amount of Grignard (equiv.)	Time of reaction	Products by GLC (by ^{1}H NMR)			Ratio (**7a**) *trans*/*cis*[a] by ^{1}H NMR
			5a	**6a**	**7a**	
EtMgBr	1.3	30 min	14 (17)	86 (83)	Trace[b]	–
	1.5	30 min	3 (3)	97 (97)	Trace[b]	–
	1.7	30 min	– (0)	100 (100)	Trace[b]	–
EtMgCl[c]	1.5	30 min	–	81	18	1.74:1
t-BuMgCl	2.0	30 min	33	16	48	–
		1 h	19	23	50	–
		24 h	12 (14)	28 (30)	55 (56)	1.41:1
i-PrMgBr	1.5	30 min	– (0)	98 (100)	1 (0)	–
$PhCH_2MgBr$	1.5	30 min	16	82[d]	Trace[b]	–
		4 h	13 (33)	85[d] (67)	Trace[b]	–
	2.0	30 min	11	84[d]	Trace[b]	–
		24 h	8 (15)	87[d] (85)	Trace[b]	–
PhMgBr	1.5	30 min	92	1	2	–
		7 h	75	2	7	–
		24 h	64 (91)	3 (3)	10 (6)	1.14:1
MeMgCl[c]	1.5	30 min	87	11	2	–
		4 h	43	51	4	–
		24 h	26 (35)	68 (60)	6 (5)	1.20:1

[a] Relative to the phenyl substituent.
[b] Less than 0.5% by GLC data.
[c] From Aldrich.
[d] Peak of (**6a**) together with benzyl bromide.

Inoue et al. that the reaction of 1,1-dibromo-2-hexylcyclopropane with butylmagnesium bromide in THF, apparently at 0°C leads efficiently to 1,2-nonadiene, although no reaction time is given, suggesting the intermediacy of the corresponding cyclopropylidene.[9] We have therefore re-examined the reaction of dibromocyclopropanes with Grignard reagents in THF.

Reaction of a number of *gem*-dibromocyclopropanes with ethylmagnesium bromide in THF at −20 to 20°C does indeed lead rapidly and efficiently to the corresponding allene (Tables 1–3). Given the practical advantages of preparing a Grignard reagent rather than an organolithium, we believe this method may offer significant benefits in allene synthesis. In a typical experiment, 1.3–2.0 mol equiv. of ethylmagnesium bromide in THF and 1.0 mol equiv. of dibromocyclopropane were stirred in dry THF under nitrogen for 30 min–1 h at room temperature. Aqueous work up gave the corresponding allene in 91–96% yield after purification (Scheme 2).

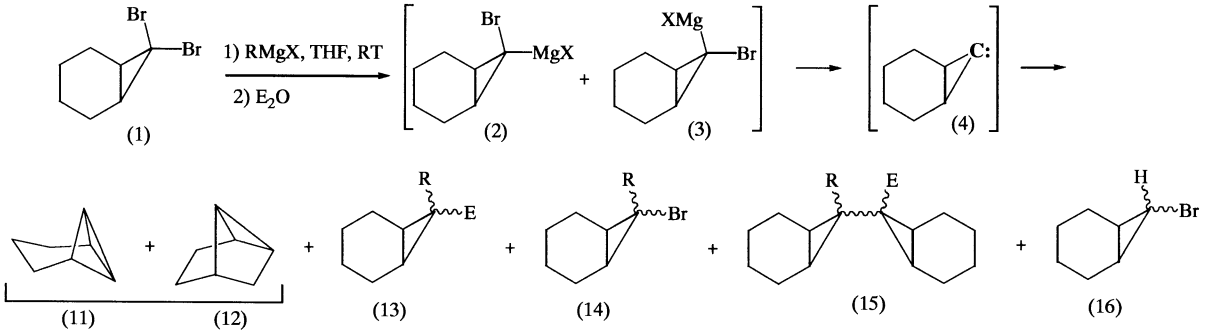
The results of these reactions are summarised in Table 1. It can be seen that an excess of the Grignard reagent was required in each case but that the allenes (**6**) were produced in each case with no more than 2% of the corresponding monobromide.

By comparison with the reaction of *gem*-dibromocyclopropanes with methyllithium described earlier, a reasonable mechanism for this reaction may involve initial magnesium bromine exchange, followed by loss of magnesium bromide to give the corresponding cyclopropylidene (or a related carbenoid) and rearrangement (Scheme 3).

The reaction of *gem*-dibromocyclopropanes with Grignard reagents was rather dependent on the exact nature of these. Thus reaction of (**5a**) with ethylmagnesium chloride in THF proceeded just as quickly as that with ethylmagnesium bromide, but was considerably less selective (Table 2). The formation of allene (**6a**) was also successful when (**5a**) was treated with prop-2-yl magnesium bromide in THF. Reaction with benzylmagnesium bromide also led to allene as the only major product, although it occurred slowly and required a large excess of the Grignard reagent (see Table 2). The reaction with *t*-butylmagnesium chloride did give allene, though not in such high yield as with the other Grignard reagents; indeed the major product was the monobromide (**7a**). However, no reaction occurred when (**5a**) was treated with phenyl magnesium bromide in THF. Unfortunately, 1,1-dichloro-2-methyl-2-phenylcyclopropane did not react with either ethyl magnesium bromide or *t*-butylmagnesium chloride in THF and only about 7% allene formation occurred when it was treated with prop-2-ylmagnesium bromide for 18 h at 20°C.

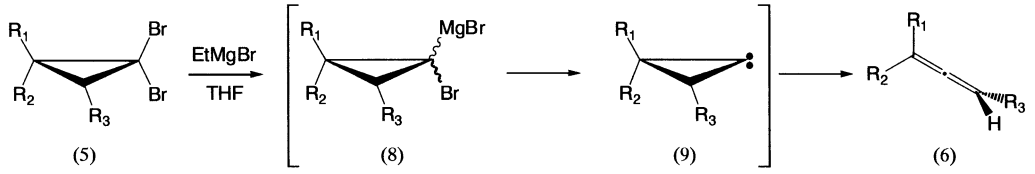
Reaction with 1.5 mol equiv. of methylmagnesium chloride in THF at ambient temperature led to incomplete reaction. After 8 h, 32% of the starting material remained and a

Table 3. Reactions of (**1**) with Grignard reagents in THF



Conditions	Products (by GLC and GC/MS data)					
	1	**11+12**	**13**[a]	**14**[b]	**15**	**16**
MeMgCl, 3 mol equiv., 24 h, rt, R=Me, E=H,D	4	4	23 *exo*/*endo* 3.0:1	20	–	45 *exo*:*endo* 1:2.0
EtMgBr, 2 mol equiv., 30 min, rt, R=Et, E=H,D	6	9	66 *exo*/*endo* 3.8:1	2	12	Trace
i-PrMgBr, 2 mol equiv., 30 min, rt, R=*i*-Pr, E=H	–	55	23 *exo*/*endo* 3.9:1	1	–	6 *exo*:*endo*1:1.9

[a] Isomers (**13**) were characterized only by MS and NMR of the mixture. The stereochemical assignment was made on the basis of relative retention times.[10]
[b] Compound (**14**) was one peak by GLC but it is not clear whether only one stereoisomer is present and, if so, which it is.



Scheme 3.

mixture of 63% allene and 3% monobromide was observed by GLC; after 24 h, the yield of allene had increased to 68%. The reaction of the dibromide (**1**) with 3 mol equiv. of methyl magnesium chloride in THF is described later.

The reaction of 7,7-dibromobicyclo[4.1.0]heptane (**1**) with methyllithium represents a classical example of a process in which allene formation from an intermediate cyclopropylidene is suppressed and alternative processes such as inter- and intramolecular insertion of the carbene into C–H bonds and formal dimerisation are observed.[1] It was of interest therefore to examine the corresponding reaction of (**1**) with ethylmagnesium bromide; this led, after aqueous work up, to a complex mixture including (**11**)–(**16**) (R=Et, E=H). The stereochemistry of (**15**) was not established. The tricycles (**11**) and (**12**) were also observed in the corresponding reaction of (**1**) with methyllithium, as was the 7-bromo-7-methyl- analogue (**14**, R=Me); however, products (**13**, R=Et, E=H) and (**15**, R=Et, E=H) appear to derive by reaction of the cyclopropylidene (**4**) with the excess of ethylmagnesium bromide to give (**13**, R=Et, E=MgBr); this in turn is either quenched on work up or reacts with a second molecule of the carbene (**4**) to give (**15**, R=Et, E=MgBr), and is in turn quenched on work up. In agreement, D_2O quenching led to the appropriate deuterated products. The requirement for an excess of Grignard reagent for complete reaction may result in such trapping of the carbene (carbenoid) whenever the latter has no favourable intramolecular process available.

The results in Table 3 suggest that the reactions of the dibromide (**1**) with simple Grignard reagents follow a common pattern; however, there are clearly significant differences in product ratio. In particular, the very high proportion of carbene insertion products (**11**) and (**12**) in the reaction with *i*-PrMgBr may be of value. The detailed explanation of these differences would require additional work.

The reaction of (**5a**) with EtMgBr in THF was then carried out at a range of temperatures; the results are given in Table 4. This clearly shows that the reaction occurred relatively quickly even at −80°C and that when the reactions were carried out and worked up at −60°C or below with a proton source, the major product was a mixture of stereoisomeric monobromides; the ratio of this mixture changed with temperature. Quenching with MeOD led to essentially complete incorporation of deuterium at C-1 of the cyclopropane.

The results in Table 4, and the incorporation of deuterium suggested that at low temperature an organomagnesium species was obtained that might be expected to be trapped by added electrophiles (Scheme 4).

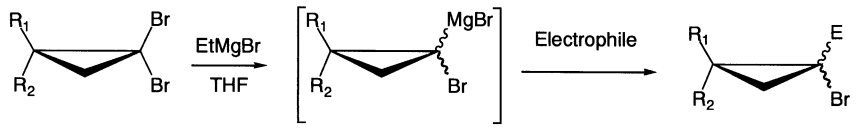
The results of such trapping experiments are shown in Table 5; in most cases with (**5b**), the major product was the monobromide and did not incorporate the electrophile; however, deuteration was efficient and trapping with iodine or carbon dioxide occurred in about 45% yield. Reaction with the dibromide (**5c**) was more efficient; in particular with carbon dioxide, the acid (**10c**, E=COOH) was obtained as a mixture of isomers in 94% yield. Acids of type (**10**) have previously been obtained from the dibromocyclopropane by reaction with an alkyllithium at low temperature followed by quenching with carbon dioxide,[11] and by other routes.[12]

Although trapping of the intermediate organomagnesium

Table 4. Effect of temperature on the reaction of (**5a**) with ethylmagnesium bromide in THF

Temperature, °C	Time of stirring, (min)	Products (by GLC)			Ratio (**7a**) *trans*/*cis*[a] by ^{1}H NMR
		5a	**7a**	**6a**	
−80	30	47	50	Trace	1:1.1
−60	30	26	70	<1	1.1:1
−60	1 h	26	69	1	1.2:1[b]
−50	30	22	68	5	2.0:1[b]
−40	30	13	61	22	3.9:1[b]
−30	30	12	10	77	2.8:1
−20	30	–	1	99	–

Work up was carried out by adding methanol at the reaction temperature.
[a] Relative to the phenyl substituent.
[b] Reaction mixture was worked up with CH_3OD to give completely deuterated monobromides.



(5) (8) (10)

	(a)	(b)	(c)	(e)
R_1	Ph	Ph	Ph	Hexyl
R_2	Me	Ph	H	H

Scheme 4.

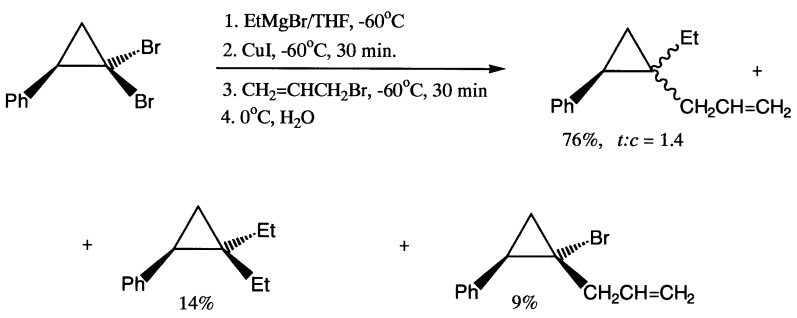
Table 5. Trapping of 1-bromomagnesio-1-bromocyclopropanes with electrophiles

Starting material	EtMgBr (mol equiv.)	Electrophile	Mol equiv.	Temperature (°C)	Time (min)	Temperature (°C)/ quenching agent	Product	Yield (%)
5b	3	Allyl bromide	5	−60	30	0, H_2O	**6b**	[a]
5b	3	$ClSiMe_3$	5	−60	60	−60, MeOH	**7b**	[a]
5b	3	$ClCO_2Me$	5	−60	60	0, MeOH	**6b**	[a]
5b	3	CH_3COCl	5	−60	30	0, MeOH	**7b**[b]	[a]
5b	3	MeOD	18	−60	–	0, H_2O	**7b**[c]	95
5b	3	$(CH_3)_2CO$	7	−60	30	0, H_2O	**7b**[d]	96
5b	3	$(CD_3)_2CO$	7	−60	30	0, H_2O	**7b**[e]	98
5b	3	Iodine	10	−60	30	0, H_2O	**10b**, E=I	47[f]
5b	3	CO_2	40	−80	60	0, H_2O/HCl	**10b**, E=COOH	46
5a	4	MeOD	7	−60	–	0, H_2O	**7a**[g]	95
5c	4	$ClSiMe_3$	7	−60	60	0, H_2O	**6c**	[a]
5c	4	MeOH	5	−60	–	0, H_2O	**7c**[h]	97
5c	4	CO_2	60	−80	60	0, H_2O/HCl	**10c**, E=COOH[i]	94
5e	3[j]	MeOH	7	−70	–	0, H_2O	**7e**[k]	97
5e	3[j]	$ClSiMe_3$	5	−70	60	0, H_2O	**6e**	[a]
5e	3[j]	CO_2	60	−80	60	0, H_2O/HCl	**10e**, E=COOH[l]	74

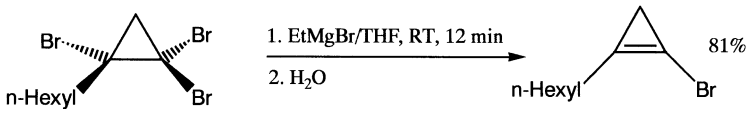
[a] Only dibromocyclopropane-derived product by NMR.
[b] The reaction mixture contained 96% of (**7b**) and 4% of (**6b**) by ^{1}H NMR. Compound (**7b**) probably formed by reaction of bromomagnesiocyclopropane with 2-butanone, which derived from reaction of excess of EtMgBr with acetyl chloride; an alternative could involve a direct elimination of hydrogen from acetyl chloride by bromomagnesiocyclopropane since the C–H acidity of the latter is higher than that of the former.
[c] (**7b**) was completely deuterated.
[d] 4-Methyl-4-hydroxy-2-pentanone was isolated as a by-product (80%, calculated on amount of (**1b**)).
[e] (**7b**) was completely deuterated, 4-methyl-4-hydroxy-2-pentanone-d_{11} was isolated as a by-product (79%, calculated on amount of (**1b**)).
[f] Yield after crystallization. The reaction mixture contained 75% 1,1-diphenyl-2-bromo-2-iodo-cyclopropane and 25% of 3,3-diphenyl-1,2-diiodoprop-2-ene (separate addition of iodine in chloroform to the allene at 20°C led to this di-iodide in 97% yield. The di-iodide in turn is converted efficiently into the corresponding 2-iodo-1-acetoxypropene by reaction with sodium acetate and this is readily hydrolysed to 3,3-diphenyl-2-iodoprop-2-en-1-ol with sodium hydroxide in aqueous ethanol[36]), the product of addition of iodine to 1,1-diphenylpropa-1,2-diene, by ^{1}H NMR.
[g] (**7a**) was completely deuterated, ratio *trans*/*cis* 1.13:1.
[h] *trans*/*cis* 1.25:1 by GLC.
[i] Isolated as methyl esters after treatment with diazomethane, *trans*/*cis* 1.4:1 by ^{1}H NMR.
[j] *i*-PrMgBr used instead of EtMgBr.
[k] *trans*/*cis* 1:1 by GLC.
[l] Isolated as methyl esters after treatment with diazomethane, *trans*/*cis* 1:1 by ^{1}H NMR.

species was very efficient with a source of H^+, D^+, or on quenching with carbon dioxide, and moderately efficient with a source of I^+, trapping with other electrophiles was not generally successful. This contrasts the trapping of 1-lithio-1-bromocyclopropanes with allylic halides,[13] trialkylchlorosilanes,[14] acetone,[15] acid chlorides,[16] or esters,[17] a number of successful examples of which are reported. It is interesting to note that the α-bromomagnesiocyclopropane (**8a**), if the intermediate does have such a structure, shows rather a unusual combination of high protophilic activity in reactions with alcohols and with acetone and acetyl chloride and a very low nucleophilic activity in reactions with the same carbonyl compounds. Reactions of compound (**5b**) with a Grignard reagent followed by acetone and d_6-acetone at −60°C for 30 min proved to be a very effective route to 4-methyl-4-hydroxy-2-pentanone (80%) or its d_{11}-analogue (79%), together with the 1-bromo-2,2-diphenylcyclopropane or 1-bromo-1-deuterio-2,2-diphenyl-cyclopropane, respectively. It is worth noting that in a traditional synthesis of 4-methyl-4-hydroxy-2-pentanone from acetone and barium hydroxide, yields are about 71% after approximately 95–120 h.[18] In an attempt to promote trapping of (**8c**) with allyl bromide, the dibromide (**5c**) was treated with 4 mol equiv. of ethylmagnesium bromide at −60°C and then with 4.25 mol equiv. of cuprous iodide followed by 8 mol equiv. of allyl bromide. This led to a mixture of 1-ethyl-1-allyl-2-phenyl-cyclopropane (76%) (*trans*/*cis* 1.4:1) together with 1,1-diethyl-2-phenylcyclo-propane (14%) and *trans*-1-bromo-1-allyl-2-phenylcyclopropane (9%) (Scheme 5).

Reaction of (**5b**) with 3 mol equiv. of EtMgBr at −60°C for



Scheme 5.



Scheme 6.

30 min (to ensure complete reaction of (**5b**)) followed by the addition of 2.5 mol equiv. of (**5a**) and stirring for a further 30 min at −60°C, gave a mixture which included by ^{1}H NMR no (**5b**) and 61% (**5a**). In the same way, reaction of (**5a**) with 4 mol equiv. of EtMgBr at −60°C for 30 min following addition of 3 mol equiv. of (**5b**) and stirring for further 30 min at −60°C gave a mixture that contained no (**5a**) and 50% (**5b**). These results suggest that there is no equilibrium between the magnesiobromocyclopropane and dibromocyclopropane as has been reported in the case of the lithiobromocyclopropanes.[7]

The reaction of 2-hexyl-1,1,2-tribromocyclopropane with 1.3 mol equiv. ethylmagnesium bromide in THF for 30 min at ambient temperature led in high yield to 1,2-debromination and the formation of 2-hexyl-1-bromocyclopropene (Scheme 6).

Similar dehalogenations have been very effectively achieved by reaction of this and related tribromides with an alkyllithium; in this case the elimination occurs rapidly even below ambient temperature and a second mol equiv. of the organolithium undergoes lithium–bromine exchange to produce a 1-lithiocyclopropene that can be trapped by a range of electrophiles.[19] Reaction of 2-hexyl-1,1,2-tribromocyclopropane with 7 mol equiv. of ethyl magnesium bromide for 3 h at ambient, followed by quenching with trimethylsilyl chloride led, in a similar process to 1-trimethylsilyl-2-hexylcyclopropene by crude ^{1}H NMR, presumably by a magnesium–bromine exchange in the intermediate bromocyclopropene; incomplete reaction occurred with fewer than 7 mol equiv. of the reagent. Given the large excess of Grignard reagent required in the present reaction, it would seem likely that an alkyllithium will remain the reagent of choice in such transformations.[19]

It is important to note that no reaction was observed between 1,1-dichlorocyclopropanes and Grignard reagents in THF even at ambient temperature. In this context, it is also worth noting that magnesium cyclopropylidenes can be generated by reaction of a 1-chlorocyclopropyl sulphoxide with Grignard reagents and that under proper conditions these can either be trapped as monochlorides after protonation, or rearrange to allenes.[20]

In summary, ethyl- and isopropylmagnesium bromide in THF are convenient reagents for highly selective and effective transformations of *gem*-dibromocyclopropanes into aliphatic and non-strained alicyclic allenes. Intermediate formation of 1-bromo-1-bromomagnesiocyclopropanes is supported by reactions with water, methanol, methanol-*d*. The α-brominated cyclopropylmagnesiobromides proved to be rather poor nucleophiles in reactions with allyl bromide, acetone, acetone-d_6, acetyl chloride, methyl chloroformate and TMSCl. Nevertheless, the reactivity of one of the α-bromocyclopropylmagnesiobromides, (**8c**), was significantly increased by transformation of this into the appropriate cuprate and 1-allyl-1-ethyl-2-phenylcyclopropane was isolated in a reasonable preparative yield.

1. Experimental

Commercial reagents were used without further purification unless stated. Magnesium was 99.98% pure from Aldrich. *gem*-Dibromocyclopropanes were prepared using standard procedure from alkenes and bromoform in two phase reactions and spectral data of these compounds were identical to those described in literature. THF was distilled over sodium wire. Petroleum ether was of boiling point 40–60°C unless stated. Reactions requiring anhydrous conditions were performed using oven dried glassware (160°C) cooled under a stream of dry nitrogen or argon; the experiments were conducted under a positive atmosphere of one of these gases. Unless stated, organic solutions were dried over anhydrous magnesium sulphate, and evaporated at 14 mmHg; yields quoted are for purified compounds and any ratios given are calculated by comparing integrals in the ^{1}H NMR spectrum. New compounds were homogeneous by GLC or TLC. GLC was conducted using a Carlo Erba HRGC 5300 (F.I.D., on a capillary column). TLC was performed using Aldrich silica plates coated with silica gel 60 (F254). Compounds were visualised using an ultraviolet source, by exposure to iodine vapour or by contact with phosphomolybdic acid hydrate (2% in ethanol) followed by heating to 180°C. Column chromatography was conducted with Fisher Scientific Silica Gel 60 under medium pressure.

Melting points are uncorrected. Infrared spectra were obtained as a solution in $CHCl_3$ or as liquid films on a Perkin–Elmer 1600 FTIR spectrometer. Low-resolution mass spectra were obtained on a Finnigan 8430 spectrometer. Microanalyses were performed on a Carlo Erba Model 1106 CHN analyser. NMR spectra were recorded in $CDCl_3$, unless stated, on a Bruker AC250 at 250 MHz for protons, at 62.9 MHz for carbons and in the latter case were either broad-band or gated decoupled. Previously described compounds were characterized by comparison with literature data using IR, ^{1}H and ^{13}C NMR where these were reported; they corresponded closely to those described except the ^{13}C NMR data for 1,1-diphenylpropa-1,2-diene.[21] Where no such data are given in the literature, they are included herein.

1.1. Preparation of allenes

Standard procedure. 1.0 M ethylmagnesium bromide in THF (13.0–20.0 ml, 13.0–20.0 mmol, 1.30–2.00 mol equiv.) was added to a stirred solution of dibromocyclopropane (10.0 mmol) in dry THF (20 ml) under nitrogen

at room temperature. Stirring was continued for 30 min–1 h when water (2 ml) was added. The organic layer was separated, the water suspension of magnesium salt was dissolved in a small amount of 4 M hydrochloric acid and extracted with petroleum (2×10 ml). The combined organic layers were dried and evaporated in vacuo. The product was treated with petroleum (5 ml), filtered through silica (5 g), washing the silica with petroleum and evaporated to give allene. The product was generally pure enough to use directly.

1.1.1. 3-Phenylbuta-1,2-diene. 1,1-Dibromo-2-methyl-2-phenylcyclopropane (2.90 g, 10.0 mmol) was treated as above with 1.0 M ethylmagnesium bromide (17.0 ml, 17.0 mmol, 1.70 mol equiv.) adding over 9 min and stirring for 30 min to give *3-phenylbuta-1,2-diene*[22] (1.26 g, 9.6 mmol, 96%) as a colourless oil, δ_C: 16.7+, 76.9−, 99.8, 125.7+, 126.6+, 128.3+, 136.7, 209.0.

1.1.2. 1,1-Diphenylpropa-1,2-diene. 1,1-Dibromo-2,2-diphenylcyclopropane (3.521 g, 10.0 mmol) was treated as above with 1.0 M ethylmagnesium bromide (13.0 ml, 1.30 mol equiv.) adding over 4 min and stirring for 30 min to give *1,1-diphenylpropa-1,2-diene*.[21] (1.849 g, 9.6 mmol, 96%) as a slightly yellow liquid (mp 4.5–5°C), δ_C: 78.1−, 127.2+, 128.4+, 136.3, 209.9.

1.1.3. Phenylpropa-1,2-diene. 1,1-Dibromo-2-phenylcyclopropane (2.760 g, 10.0 mmol) was treated as above with 1.0 M ethylmagnesium bromide (13.0 ml, 13.0 mmol, 1.30 mol equiv.) adding over 5 min and stirring for 30 min to give *phenylpropa-1,2-diene*[23] (1.068 g, 9.2 mmol, 92%) as a colourless liquid.

1.1.4. Cyclonona-1,2-diene. 9,9-Dibromobicyclo[6,1,0]-nonane (2.820 g, 10.0 mmol) was treated as above with 1.0 M ethylmagnesium bromide (20.0 ml, 20.0 mmol, 2.0 mol equiv.) adding over 4 min and stirring for 1 h to give *cyclonona-1,2-diene*[24] (1.14 g, 9.3 mmol, 93%) as a colourless oil.

1.1.5. Nona-1,2-diene. 1,1-Dibromo-2-hexylcyclopropane (2.840 g, 10.0 mmol) was treated as above with 1.0 M ethylmagnesium bromide (17.0 ml, 17.0 mmol, 1.70 mol equiv.) adding over 12 min and stirring for 1 h to give *nona-1,2-diene*[25] (1.129 g, 9.1 mmol, 91%) as a colourless liquid.

1.2. Generation of 1-bromo-1-bromomagnesiocyclopropanes

Standard procedure. 1.0 M ethylmagnesium bromide or 0.8 M isopropylmagnesium bromide in THF (9.0–12.0 mmol, 3.00–4.00 mol equiv.) was added to a stirred solution of the dibromocyclopropane (3.0 mmol) in dry THF (6–30 ml) under nitrogen at −60±1 or −70±1°C. Stirring was continued for 30 min at the same temperature to give the solution of 1-bromomagnesio-1-bromocyclopropane.

1.3. Reactions of 1,1-dibromo-2-methyl-2-phenylcyclopropane with Grignard reagents

Standard procedure. A 1.0 M solution of a Grignard reagent in THF (4.5–6.0 ml, 4.5–6.0 mmol, 1.50–2.00 mol equiv.) was added to a stirred solution of 1,1-dibromo-2-methyl-2-phenylcyclopropane (870 mg, 3.0 mmol) in dry THF (6 ml) under nitrogen at room temperature. Stirring was continued for 30 min–24 h at room temperature when water (0.5 ml) was added. The organic layer was separated, the water suspension of magnesium salt was dissolved in a small amount of 4 M hydrochloric acid and extracted with petroleum (2×5 ml). The combined organic layers were dried and evaporated. The product was analysed by ^{1}H NMR. The reactions were monitored by removing samples (0.1 ml) for GLC at 30 min, 1, 2, 4, 8 and 24 h. The results of these experiments are presented in Table 2.

1.4. A study of the stability of 1-bromomagnesio-1-bromo-2-methyl-2-phenylcyclopropane

1.0 M ethylmagnesium bromide in THF (5.1 ml, 5.1 mmol, 1.70 mol equiv.) was added to a stirred solution of 1,1-dibromo-2-methyl-2-phenylcyclopropane (870 mg, 3.0 mmol) in dry THF (6 ml) under nitrogen at the appropriate temperature. Stirring was continued for 30 min at that temperature when methanol or methanol-*O-d* (2 ml) was slowly added. The resulting solution was warmed to 0°C and water (0.5 ml) was added. The mixture was diluted with petroleum to 50 ml, dried, analysed by GLC and evaporated to give an oil, which was analysed by ^{1}H NMR. The conditions and results of these experiments are given in Table 4.

1.5. Reactions of 1-bromomagnesio-1-bromocyclopropanes with electrophiles

1.5.1. 1-Bromomagnesio-1-bromo-2,2-diphenylcyclopropane. (i) *With CH_3OD*. 1-Bromomagnesio-1-bromo-2,2-diphenylcyclopropane was prepared as above using 1,1-dibromo-2,2-diphenylcyclopropane (704 mg, 2.0 mmol), THF (4 ml) and 1.0 M ethylmagnesium bromide (6 ml, 6.0 mmol, 3.00 mol equiv.) at −60°C. The reaction mixture was cooled to −80°C and methanol-*O-d* (1 ml) was slowly added at not above −60°C. The reaction mixture was warmed to 0°C and water (0.5 ml) was added. The resulting solution was diluted with ether to 75 ml, dried and evaporated in vacuo to give a solid, which was filtered through silica (1 g) washing with petroleum to give *1,1-diphenyl-2-bromo-2-deuteriocyclopropane* (522 mg, 1.9 mmol, 95%) as a white solid (mp 77–79°C) (Calculated for $C_{15}H_{12}BrD$: C 65.71; H 5.15%. Found: C 65.8; H 4.9%), δ_H: 1.85 (1H, d, J=6.4 Hz), 1.90 (1H, d, J=6.4 Hz), 7.16–7.48 (10H, m); δ_C: 23.9−, 28.1 (t, J=28.6 Hz), 36.2, 126.7+, 127.0+, 127.8+, 128.3+, 128.6+, 130.5+, 140.7, 144.2; IR (cm^{-1}, in $CHCl_3$): 1599 m, 1494 s, 1446 s, 1069 m, 1014 m, 702 s.

(ii) *With acetone*. 1-Bromomagnesio-1-bromo-2,2-diphenylcyclopropane was prepared as in (i). A solution of acetone (1 ml) in dry THF (1 ml) was added at −60°C and stirring was continued for 30 min at the same temperature. The mixture was warmed to 0°C and water (1 ml) was added. The resulting solution was diluted with ether to 50 ml, dried and evaporated to give product (880 mg), which was separated by column chromatography on silica (40 g) eluting with 3:2 petroleum/ether to give *1-bromo-2,2-diphenyl-*

cyclopropane[26] (522 mg, 1.91 mmol, 96%) as a white solid (mp 77–79°C) which showed δ_H: 1.85 (1H, dd, J=6.4, 5.2 Hz), 1.89 (1H, dd, J=7.6, 6.4 Hz), 3.78 (1H, dd, J=7.6, 5.2 Hz), 7.13–7.46 (10H, m); δ_C: 24.0−, 28.5+, 36.4, 126.8+, 127.2+, 127.8+, 128.3+, 128.7+, 130.6+, 140.8, 144.2; IR (cm^{-1}, in $CHCl_3$): 1598 m, 1494 s, 1445 s, 1423 m, 1314 m, 1079 m, 918 m, 703 s, 633 m, 604 m; and 4-hydroxy-4-methylpentan-2-one[27] (186 mg, 1.60 mmol, 80%) as a colourless liquid which showed IR (cm^{-1}, film): 3442 br.s, 2974 s, 2933 m, 1702 s, 1418 m, 1408 m, 1378 s, 1364 s, 1333 m, 1217 m, 1180 m, 1147 m, 915 m, 734 m.

(iii) *With acetone-d_6*. The above experiment was repeated except that acetone was replaced by acetone-d_6 to give crude product (880 mg), which was separated by column chromatography on silica (40 g) eluting with 3:2 petroleum/ether to give *1-bromo-2,2-diphenyl-1-deuteriocyclopropane* (539 mg, 1.97 mmol, 98%) as a white solid (mp 77–79°C) with spectral data identical to above and *4-hydroxy-4-methylpentan-2-one-d_{11}* (201 mg, 1.58 mmol, 79%) as a colourless liquid which showed δ_H: 3.58 (1H, broad s); δ_C: 28.3 (septet, J=19.1 Hz), 31.3 (septet, J=19.1 Hz), 53.5 (pentet, J=19.1 Hz), 68.9, 210.8; IR (cm^{-1}, film): 3452 br.s, 2229 s, 1696 s, 1384 br.s, 1257 br.s, 1204 br.s, 1153 br.s, 1096 m, 1053 s, 818 s.

(iv) *With trimethylchlorosilane*. 1-Bromomagnesio-1-bromo-2,2-diphenylcyclopropane was prepared as in (i). Then a solution of trimethylchlorosilane (1.086 g, 1.27 ml, 10 mmol, 5 mol equiv.) in dry THF (0.7 ml) was added at the same temperature and stirring was continued for 60 min. The mixture was cooled to −80°C and methanol (1.5 ml) was slowly added at not above −60°C. It was then warmed to 0°C and water (1 ml) was added. The organic layer was separated, the water suspension of magnesium salt was dissolved in a small amount of 4 M hydrochloric acid and extracted with ether (3×5 ml). The combined organic layers were dried and evaporated to give an oil, which contained only 1-bromo-1,1-diphenylcyclopropane derived from the cyclopropane, by ^{1}H NMR.

(v) *With allyl bromide*. 1-Bromomagnesio-1-bromo-2,2-diphenylcyclopropane was prepared as in (i). Then a solution of allylbromide (1.210 g, 0.87 ml, 10 mmol, 5 mol equiv.) in dry THF (1 ml) was added at −60°C and stirring was continued for 30 min at the same temperature. The mixture was warmed to 0°C for 40 min and water (1 ml) was added. The resulting solution was diluted with ether to 75 ml, dried and evaporated to give an oil, which contained only 1,1-diphenylpropa-1,2-diene by ^{1}H NMR.

(vi) *With methyl chloroformate*. 1-Bromomagnesio-1-bromo-2,2-diphenylcyclopropane was prepared as in (i). Then a solution of methyl chloroformate (945 mg, 0.77 ml, 10 mmol, 5 mol equiv.) in dry THF (1.2 ml) was added at the same temperature and stirring was continued for 60 min. The mixture was warmed to 0°C for 40 min and methanol (1.5 ml) was added. After 15 min water (0.5 ml) was added. The resulting solution was diluted with ether to 50 ml, dried and evaporated to give an oil, which by ^{1}H NMR contained only 1,1-diphenylpropa-1,2-diene derived from cyclopropane.

(vii) *With acetyl chloride*. 1-Bromomagnesio-1-bromo-2,2-diphenylcyclopropane was prepared as in (i). Then a solution of acetyl chloride (785 mg, 0.71 ml, 10 mmol, 5 mol equiv.) in dry THF (1.3 ml) was added at −60°C and stirring was continued for 30 min. The reaction mixture was warmed to 0°C over 50 min and methanol (1.5 ml) was added followed after 15 min by water (0.5 ml). The resulting solution was diluted with ether to 40 ml, dried and evaporated to give an oil, which contained only 1-bromo-2,2-diphenylcyclopropane (96%) and 1,1-diphenylpropa-1,2-diene (4%) derived from cyclopropane by ^{1}H NMR.

(viii) *With iodine*. 1-Bromomagnesio-1-bromo-2,2-diphenylcyclopropane was prepared as in (i). A solution of iodine (5.076 g, 20 mmol, 10 mol equiv.) in dry THF (16 ml) was added at −60°C and stirring was continued for 30 min at the same temperature. The mixture was warmed to 0°C for 40 min, poured into chloroform (100 ml) and washed with sat. aq. sodium thiosulphate (40 ml). The organic layer was separated and the water layer extracted with chloroform (3×20 ml). The combined organic layers were dried and evaporated to give a solid (783 mg), which contained 25% 3,3-diphenyl-1,2-di-iodoprop-2-ene (given later) and 75% 1-bromo-1-iodo-2,2-diphenyl-cyclopropane by ^{1}H NMR. The solid was crystallized from hexane (20 ml) to give pure *1-bromo-1-iodo-2,2-diphenylcyclopropane* (376 mg, 0.94 mmol, 47%) as a white solid (mp 156–158°C (dec.)) (Calculated for $C_{15}H_{12}BrI$: C 45.15; H 3.03%. Found C 45.1; H 2.9%) which shown δ_H: 2.52 (1H, d, J=7.4 Hz), 2.60 (1H, d, J=7.4 Hz), 7.20–7.37 (6H, m), 7.49–7.57 (4H, m); δ_C: −5.7, 36.0−, 44.4, 127.3+, 127.4+, 128.4+, 128.5+, 129.0+, 129.5+, 141.4, 144.3; IR (cm^{-1}, in $CHCl_3$): 1492 s, 1446 s, 1057 s, 1001 m, 994 m, 706 s, 691 m, 629 m.

(ix) *With CO_2*. 1-Bromomagnesio-1-bromo-2,2-diphenylcyclopropane was prepared as above using 1,1-dibromo-2,2-diphenylcyclopropane (1.056 g, 3.0 mmol), dry THF (20 ml) and 1.0 M ethylmagnesium bromide (9 ml, 9.0 mmol, 3.00 mol equiv.) at −60°C. The reaction mixture was cooled to −90°C and dry CO_2 was passed in for 10 min (rate 280 ml/min, 2.8 l, 125 mmol, 40 mol equiv.) and stirring was continued for 60 min at −80°C. The reaction mixture was warmed to 0°C for 100 min, poured into chloroform (50 ml) and washed with a solution of concentrated hydrochloric acid (20 ml) in water (100 ml). The organic layer was separated and the water layer was extracted with chloroform (3×15 ml). The combined organic layers were extracted with sat. aq. sodium bicarbonate (3×15 ml) and the combined aqueous layers were extracted with chloroform (10 ml). Concentrated hydrochloric acid was added until pH 1 and the mixture was extracted with chloroform (4×15 ml). The combined organic layers were dried and evaporated to give *1-bromo-2,2-diphenylcyclopropanecarboxylic acid*[28] (436 mg, 1.37 mmol, 46%) as white solid (mp 179.5–181°C (dec); lit. mp 185–188°C) which showed δ_H: 2.11 (1H, d, J=6.6 Hz), 2.75 (1H, d, J=6.6 Hz), 7.22–7.51 (10H, m), 10.98 (1H, br.s); δ_C(acetone-d_6): 28.2, 39.6, 45.5, 127.8, 127.9, 129.1, 129.2, 129.4, 130.4, 141.8, 143.0, 168.9; IR (cm^{-1}, in $CHCl_3$): 3064 br.m, 3023 br.m, 2873 br.m, 2664 br.m, 2524 br.m, 1687 s, 1268 s, 744 s, 705 s.

(x) *With 1,1-dibromo-2-methyl-2-phenylcyclopropane*. 1-Bromomagnesio-1-bromo-2,2-diphenylcyclopropane was prepared as above using 1,1-dibromo-2,2-diphenylcyclopropane (352 mg, 1.0 mmol), dry THF (2 ml) and 1.0 M ethylmagnesium bromide (3 ml, 3.0 mmol, 3.00 mol equiv.) at −60°C. Then a solution of 1,1-dibromo-2-methyl-2-phenylcyclopropane (725 mg, 2.5 mmol, 2.5 mol equiv.) in dry THF (3 ml) was added at −60°C and stirring was continued for 30 min at the same temperature. The mixture was cooled to −80°C while methanol (1.5 ml) was slowly added at not more than −60°C, and then warmed to 0°C and water (1 ml) was added. The resulting solution was diluted with ether to 50 ml, dried and evaporated to give an oil, which contained 1-bromo-2,2-diphenylcyclopropane (31%), 1,1-dibromo-2-methyl-2-phenylcyclopropane (62%) and 1-bromo-2-methyl-2-phenyl cyclopropane (7%, *trans*/*cis* 1.13:1) by ^{1}H NMR.

1.5.2. 1-Bromomagnesio-1-bromo-2-methyl-2-phenylcyclopropane. (i) *With CH_3OD*. 1-Bromomagnesio-1-bromo-2-methyl-2-phenylcyclopropane was prepared as above using 1,1-dibromo-2-methyl-2-phenylcyclopropane (870 mg, 3.0 mmol), dry THF (6 ml) and 1.0 M ethylmagnesium bromide (12 ml, 12.0 mmol, 4.00 mol equiv.) at −60°C. The reaction mixture was cooled to −80°C and methanol-*O*-*d* (1 ml) was slowly added at not more than −60°C. The mixture was warmed to 0°C and water (1 ml) was added. The organic layer was separated, the water suspension of magnesium salt was dissolved in a small amount of 4 M hydrochloric acid and extracted with petroleum (3×10 ml). The combined organic layers were dried and evaporated in vacuo. The product was treated with petroleum (2 ml), filtered through silica (1.5 g), washing the silica with petroleum, and evaporated to give *1-bromo-1-deuterio-2-methyl-2-phenylcyclopropane* (604 mg, 2.85 mmol, 95%, *trans*/*cis* 1.13:1 by ^{1}H NMR data) as a colourless liquid (Calculated for $C_{10}H_{10}BrD$: C, 56.63; H, 5.70%. Found: C, 56.4; H, 5.4%) which showed (*trans* isomer) δ_H: 1.09 (1H, d, J=6.4 Hz), 1.63 (3H, s), 1.65 (1H, d, J=6.4 Hz), 7.19–7.82 (5H, m); δ_C: 23.2−, 23.9+, 25.7, 30.3 (t, J=29.2 Hz), 126.5+, 127.0+, 128.6+, 144.5; (*cis* isomer) δ_H: 1.38 (1H, d, J=6.5 Hz), 1.41 (1H, d, J=6.5 Hz), 1.48 (3H, s), 7.26–7.46 (5H, m); δ_C: 22.0−, 26.9+, 27.5, 28.3 (t, J=14.5 Hz), 126.8+, 128.2+, 129.4+, 142.2; IR (cm^{-1}, film, mixture of isomers): 3059 m, 3025 m, 2959 m, 1602 m, 1497 m, 1445 s, 1074 m, 1061 m, 1027 m, 764 s, 730 m, 699 s.

(ii) *With 1,1-dibromo-2,2-diphenylcyclopropane*. 1-Bromomagnesio-1-bromo-2-methyl-2-phenylcyclopropane was prepared as in (i) above using 1,1-dibromo-2-methyl-2-phenylcyclopropane (290 mg, 1.0 mmol), dry THF (2 ml) and 1.0 M ethylmagnesium bromide (4 ml, 4.0 mmol, 4.00 mol equiv.) at −60±1°C. Then a solution of 1,1-dibromo-2,2-diphenylcyclopropane (1.056 g, 3.0 mmol, 3.0 mol equiv.) in dry THF (3 ml) was added at −60±1°C and stirring was continued for 30 min at the same temperature. The mixture was cooled to −80°C and methanol (1.5 ml) was slowly added at not more than −60°C. The mixture was warmed to 0°C and water (0.5 ml) was added. The resulting solution was diluted with ether to 50 ml, dried and evaporated to give an oil, which contained 1-bromo-2,2-diphenylcyclopropane (27%), 1,1-dibromo-2,2-diphenylcyclopropane (50%) and 1-bromo-2-methyl-2-phenylcyclopropane (23%, *trans*/*cis* 1.38:1) by ^{1}H NMR.

1.5.3. 1-Bromomagnesio-1-bromo-2-phenylcyclopropane. (i) *With CH_3OH*. 1-Bromomagnesio-1-bromo-2-phenylcyclopropane was prepared as above using 1,1-dibromo-2-phenylcyclopropane (828 mg, 3.0 mmol), dry THF (6 ml) and 1.0 M ethylmagnesium bromide (12 ml, 12.0 mmol, 4.00 mol equiv.) at −60°C. The reaction mixture was cooled to −80°C and methanol (1 ml) was slowly added at not more than −60°C. The mixture was warmed to 0°C and water (1 ml) was added. The organic layer was separated, the water suspension of magnesium salt was dissolved in a small amount of 4 M hydrochloric acid and extracted with pentane (3×10 ml). The combined organic layers were dried and evaporated in vacuo. The product was treated with pentane (2 ml), filtered through silica (1.5 g), washing the silica with pentane and evaporated to give *1-bromo-2-phenylcyclopropane*[29] (574 mg, 2.91 mmol, 97%, *trans*/*cis* 1.25:1 by GLC data) as a colourless liquid which showed IR (cm^{-1}, film): 1604 m, 1499 m, 1455 m, 1261 m, 1234 m, 763 m, 696 s.

(ii) *With trimethylchlorosilane*. 1-Bromomagnesio-1-bromo-2-phenylcyclopropane was prepared as in (i). A solution of trimethylchlorosilane (2.173 g, 2.54 ml, 20 mmol, 6.67 mol equiv.) in dry THF (1.5 ml) was added at −60°C and stirring was continued for 60 min at the same temperature. The mixture was warmed to 0°C for 90 min and water (3 ml) was added. The organic layer was separated and extracted with petroleum (3×10 ml). The combined organic layers were dried and evaporated to give oil, which contained only 1-phenylallene by ^{1}H NMR derived from cyclopropane.

(iii) *With CO_2*. 1-Bromomagnesio-1-bromo-2-phenylcyclopropane was prepared as above using 1,1-dibromo-2-phenylcyclopropane (552 mg, 2.0 mmol), dry THF (10 ml) and 1.0 M ethylmagnesium bromide (8 ml, 8.0 mmol, 4.00 mol equiv.) at −60°C. The mixture was cooled to −90°C, and dry CO_2 was passed in for 10 min (rate 300 ml/min, 3 l, 130 mmol, 65 mol equiv.) and stirring was continued for 60 min at −80°C. The mixture was warmed to 0°C for 100 min, poured into chloroform (40 ml) and washed with conc. hydrochloric acid (10 ml) in water (50 ml). The organic layer was separated and the water layer was extracted with chloroform (3×10 ml). The combined organic layers were extracted with sat. aq. sodium bicarbonate (4×15 ml); the combined layers were washed with chloroform (2×10 ml). Concentrated hydrochloric acid was added until pH 1 and they were extracted with chloroform (4×20 ml). The combined organic layers were dried and evaporated in vacuo to give an oil, which was dissolved in ether (2 ml), treated with diazomethane until a yellow colour persisted, dried and evaporated to give *methyl 1-bromo-2-phenylcyclopropanecarboxylate*[30] (480 mg, 1.88 mmol, 94%, *trans*/*cis* 1.4:1 by ^{1}H NMR data) as a colourless liquid which showed δ_C: 22.2−, 24.0−, 31.3, 33.5+, 35.0, 36.8+, 53.0+, 53.7+, 127.4+, 127.6+, 128.1+, 128.2+, 128.7+, 129.4+, 134.4, 135.6, 167.4, 170.5.

(iv) *With copper (I) iodide and allyl bromide*. 1-Bromomagnesio-1-bromo-2-phenyl-cyclopropane was prepared as above using 1,1-dibromo-2-phenylcyclopropane (221

mg, 0.8 mmol), dry THF (1.2 ml) and 1.0 M ethylmagnesium bromide (3.2 ml, 3.2 mmol, 4.00 mol equiv.) at −60°C. Copper (I) iodide (647 mg, 3.4 mmol, 4.25 mol equiv.) was added at temperature −60°C and stirring was continued for 30 min at that temperature. A solution of allyl bromide (774 mg, 0.55 ml, 6.4 mmol, 8.00 mol equiv.) in dry THF (0.45 ml) was added at −60±1°C and stirring was continued for 30 min at that temperature. The mixture was warmed to 0°C for 180 min, then water (0.5 ml) was added and the resulting suspension was diluted with petroleum to 20 ml. Magnesium sulphate (1 g) was added and solution decanted, the solid was washed with petroleum (2×10 ml). The combined organic layers were dried and evaporated to give a colourless liquid (129 mg) which contained 1,1-diethyl-2-phenylcyclopropane (14%), 1-ethyl-1-allyl-2-phenylcyclopropane (76%, *trans*/*cis* 1.4:1 by GLC) and *trans*-1-bromo-1-allyl-2-phenyl-cyclopropane (9%) by GLC. Part of this (110 mg) was separated by column chromatography on silica eluting with petroleum to give *1,1-diethyl-2-phenylcyclopropane* (6 mg) which showed δ_H: 0.70–0.90 (6H, m), 1.01 (3H, t, J=7.3 Hz), 1.15–1.29 (2H, m), 1.64 (1H, dd, J=14.6, 7.3 Hz), 1.92 (1H, dd, J=7.9, 6.1 Hz), 7.17–7.30 (5H, m); (*m*/*z*, %): 175 (2, M^++1), 174 (14, M^+), 146 (14), 145 (100), 130 (16), 128 (16), 117 (36), 115 (12), 105 (10), 104 (55), 91 (32), 77 (28), 65 (15), 55 (21), 51 (22), *trans-1-bromo-1-allyl-2-phenylcyclopropane*[31] (10 mg) and *1-allyl-1-ethyl-2-phenyl-cyclopropane* (50 mg) which showed δ_H: 0.78–1.35 (7H, m), 1.51–1.75 (1H, m), 1.92–2.44 (2H, m), 4.89–5.00 (1H, m), 5.08–5.20 (1H, m), 5.62–6.05 (1H, m), 7.16–7.34 (5H, m); δ_C: 10.5+, 10.7+, 15.9−, 16.4−, 23.6−, 27.8, 28.7+, 29.0+, 30.1−, 34.9−, 41.2−, 115.6−, 116.2−, 125.5+, 125.6+, 127.8+, 127.9+, 129.0+, 136.5+, 136.8+, 139.7; IR (cm^{-1}, film): 3061 m, 3025 m, 2995 m, 2962 s, 2921 m, 2873 m, 995 m, 910 s, 734 s, 698 s; (*m*/*z*, %) (*trans* isomer) (R_t 11.3 min): 186 (1, M^+), 171 (1), 146 (13), 145 (100), 129 (41), 117 (33), 115 (19), 105 (12), 104 (51), 91 (49), 77 (33), 67 (26), 65 (16), 53 (15), 51 (19); (*m*/*z*, %) (*cis* isomer) (R_t 11.33 min): 186 (1, M^+), 146 (13), 145 (100), 129 (43), 117 (33), 115 (30), 104 (62), 91 (63), 77 (49), 67 (37), 65 (16), 63 (13), 53 (22), 51 (21). The isomers were inseparable by column chromatography.

1.5.4. 1-Bromomagnesio-1-bromo-2-hexylcyclopropane. (i) *With CH_3OH*. 1-Bromomagnesio-1-bromo-2-hexylcyclopropane was prepared as above using 1,1-dibromo-2-hexylcyclopropane (852 mg, 3.0 mmol), dry THF (6 ml) and 0.8 M isopropylmagnesium bromide (11.25 ml, 9.0 mmol, 3.00 mol equiv.) at −70°C. The reaction mixture was cooled to −90°C and methanol (1 ml) was slowly added at not more than −70°C. The mixture was warmed to 0°C and water (1 ml) was added. The organic layer was separated, the water suspension of magnesium salt was dissolved in a small amount of 4 M hydrochloric acid and extracted with pentane (3×10 ml). The combined organic layers were dried and evaporated. The product was treated with pentane (2 ml), filtered through silica (1.5 g), washing the silica with pentane and evaporated to give *1-bromo-2-hexylcyclopropane*[31,32] (595 mg, 2.90 mmol, 97%, *trans*/*cis* 1:1 by GLC) as a colourless liquid.

(ii) *With trimethylchlorosilane*. 1-Bromomagnesio-1-bromo-2-hexylcyclopropane was prepared as above using 1,1-dibromo-2-hexylcyclopropane (568 mg, 2.0 mmol), dry THF (4 ml) and 0.8 M isopropylmagnesium bromide (7.5 ml, 6.0 mmol, 3.00 mol equiv.) at −70°C. A solution of trimethylchlorosilane (1.086 g, 1.27 ml, 10 mmol, 5.0 mol equiv.) in dry THF (0.73 ml) was added at −70°C and stirring was continued for 60 min at the same temperature. The mixture was warmed to 0°C for 60 min and water (2 ml) was added. The organic layer was separated and the water layer was extracted with petroleum (3×10 ml). The combined organic layers were dried and evaporated to give an oil, which contained by ^{1}H NMR only nona-1,2-diene derived from cyclopropane.

(iii) *With CO_2*. 1-Bromomagnesio-1-bromo-2-hexylcyclopropane was prepared as in (ii). The mixture was cooled to −90°C, dry CO_2 was passed in for 10 min (rate 300 ml/min, 3 l, 130 mmol, 65 mol equiv.) and stirring was continued for 60 min at −80°C. The mixture was warmed to 0°C for 100 min, poured in chloroform (40 ml) and washed with a solution of concentrated hydrochloric acid (10 ml) in water (50 ml). The organic layer was separated and the water layer was extracted with chloroform (3×10 ml). The combined organic layers were extracted with sat. aq. sodium bicarbonate (4×15 ml); the combined sodium bicarbonate layers were extracted with chloroform (2×10 ml), treated with concentrated hydrochloric acid until pH 1 and extracted with chloroform (4×20 ml). The combined organic layers were dried and evaporated to give an oil, which was dissolved in ether (2 ml), treated with diazomethane until the yellow colour persisted, dried with magnesium sulphate and evaporated in vacuo to give *methyl 2-bromo-1-hexylcyclopropanecarboxylate* (190 mg, 0.72 mmol, 36%, *trans*/*cis* 1:1 by ^{1}H NMR) as a colourless liquid (Calculated for $C_{11}H_{19}BrO_2$: C 50.20; H 7.28%. Found C 50.5; H 7.4%) which showed δ_H: 0.82–0.94 (3H, m), 1.02 (1H, first isomer, dd, J=7.3, 5.5 Hz), 1.20–1.89 (13H, m), 3.73 (3H, s, first isomer), 3.75 (3H, s, second isomer); δ_C: 13.9+, 14.0+, 22.47−, 22.52−, 24.6−, 26.3−, 27.6−, 28.6−, 28.7−, 28.90−, 28.93−, 29.6, 31.6−, 31.7−, 34.1+, 34.4+, 53.1+, 53.3+, 169.3, 171.1; IR (cm^{-1}, film): 2954 s, 2926 s, 2856 m, 1744 s, 1723 s, 1210 s, 1126 m. The combined organic layers from neutral fractions were washed with 10% aqueous sodium hydroxide (3×10 ml); the combined sodium hydroxide layers were extracted with dichloromethane (2×10 ml), treated with hydrochloric acid until pH 1 and extracted with dichloromethane (3×10 ml). The combined organic layers were dried and evaporated in vacuo to give an oil. This was dissolved in ether (2 ml), treated with diazomethane until the yellow colour persisted, dried with magnesium sulphate and evaporated to give *methyl 1-bromo-2-hexylcyclopropanecarboxylate* (200 mg, 0.76 mmol, 38%, *trans*/*cis* 1:1 by ^{1}H NMR data) as a colourless liquid with spectral data identical to those above (total 390 mg, 1.48 mmol, 74%, *trans*/*cis* 1:1 by ^{1}H NMR.

1.5.5. Reactions of 7,7-dibromonorcarane with Grignard reagents in THF. (a) *With methylmagnesium chloride*. 1.0 M Methylmagnesium chloride in THF (12.0 ml, 12.0 mmol, 3.00 mol equiv.) was added to a stirred solution of 7,7-dibromobicylo[4,1,0]heptane (1.016 g, 4.0 mmol) in dry THF (8 ml) under nitrogen at room temperature. Stirring was continued for 24 h at room temperature when 5 ml of

reaction mixture was worked up with D_2O (2 ml). This sample contained by GLC and GC/MS, tricyclo[4.1.0.0^{2,7}]-heptane[33] and tricyclo[3.2.0.0^{2,7}]heptane[34] (4%, R_t 2.30 and 2.48 min) which showed (*m/z*, %): 94 (33, M^+), 93 (18), 91 (16), 79 (100), 77 (37), 62 (9), 61 (10), 56 (11); *7-methyl-7-deuteriobicylo[4,1,0]heptane* (23%, *exo*-**13** (R=Me, E=D)/*endo*-**13** (R=Me, E=D)=3.0:1, R_t (*exo*-**13** (R=Me, E=D)) 3.22 min, (*endo*-**13** (R=Me, E=D)) 4.17 min) which showed (*m/z*, %): 111 (99, M^+), 96 (46), 82 (42), 81 (100), 78 (5), 77 (6), 70 (18), 69 (47), 68 (57), 67 (53); 7-bromobicyclo[4,1,0]heptane[31] (45%, *exo*-**16**/*endo*-**16**= 1:2.0, R_t (*exo*-**16**) 6.57 min, (*endo*-**16**) 7.30 min), 7-bromo-7-methylbicyclo[4,1,0]heptane[31] (20%) which showed (*m/z*, %): 190 (15, M^+, ^{81}Br), 188 (15, M^+, ^{79}Br), 148 (18), 146 (18), 135 (6), 133 (6), 109 (100), 81 (15), 79 (13), 77 (6), 68 (18), 67 (37) and 7,7-dibromobicyclo[4,1,0]-heptane (4%). The rest of the reaction mixture was worked up with water and contained by GLC and GC/MS tricyclo[4.1.0.0^{2,7}]heptane[33] and tricyclo[3.2.0.0^{2,7}]heptane[34] with spectral data identical to those above, 7-methylbicyclo[4,1,0]heptane (23%, *exo*-**13** (R=Me, E=H)/*endo*-**13** (R=Me, E=H)=3.0:1, R_t (*exo*-**13** (R=Me, E=H)) 3.22 min, (*endo*-**13** (R=Me, E=H)) 4.17 min) which showed (*m/z*, %): 110 (57, M^+), 95 (29), 82 (29), 81 (100), 68 (59), 67 (78); 7-bromobicyclo[4,1,0]heptane[31] (45%, *exo*-**16**/*endo*-**16**=1:2.0, R_t (*exo*-**16**) 6.57 min, (*endo*-**16**) 7.30 min), 7-bromo-7-methyl-bicyclo[4,1,0]heptane[31] (20%) with spectral data identical as above and 7,7-dibromo-bicyclo-[4,1,0]heptane[35] (4%). The components were inseparable by column chromatography.

(b) *With ethylmagnesium bromide (work up with H_2O).* 1.0 M Ethylmagnesium bromide in THF (10.0 ml, 10.0 mmol, 2.00 mol equiv.) was added to a stirred solution of 7,7-dibromobicylo[4,1,0]heptane (1.270 g, 5.0 mmol) in dry THF (10 ml) under nitrogen at room temperature. Stirring was continued for 30 min at room temperature when water (1 ml) was added. The reaction mixture contained by GLC and GC/MS 7,7-dibromobicylo[4,1,0]-heptane[35] (6%), 7-ethylbicylo[4,1,0]heptane (66%, *exo*-**13** (R=Et, E=H)/*endo*-**13** (R=Et, E=H)=3.8:1, R_t (*exo*-**13** (R=Et, E=H)) 3.48 min, (*endo*-**13** (R=Et, E=H)) 4.26 min) which showed (*m/z*, %): 124 (12, M^+), 109 (4), 96 (7), 95 (41), 83 (9), 81 (72), 79 (16), 77 (11), 68 (24), 67 (83), 54 (100); tricyclo[4.1.0.0^{2,7}]heptane[33] and tricyclo[3.2.0.0^{2,7}]heptane[34] (9%, R_t 2.16 min) with spectral data identical as above, 7-bromo-7-ethyl-bicylo[4,1,0]-heptane (2%, R_t 7.30 min) which showed (*m/z*, %): 204 (3, M^+, ^{81}Br), 202 (3, M^+, ^{79}Br), 162 (2), 160 (2), 123 (18), 108 (2), 96 (7), 94 (7), 81 (92), 67 (100), 55 (39) and 7-ethyl-(7,7′)-bi(bicyclo[4,1,0]heptyl) (12%, R_t 11.13 and 11.32 min) which showed (*m/z*, %) for isomer with R_t 11.13: 218 (2, M^+), 189 (54), 175 (5), 162 (6), 148 (16), 135 (32), 132 (10), 122 (31), 119 (14), 108 (56), 96 (22), 94 (34), 92 (22), 81 (38), 79 (100), 67 (59), 55 (39); (*m/z*, %) for isomer with R_t 11.32: 218 (4, M^+), 189 (77), 176 (18), 149 (10), 147 (7), 136 (14), 134 (14), 132 (10), 121 (64), 118 (11), 108 (64), 106 (25), 96 (34), 93 (53), 81 (25), 79 (87), 67 (56), 55 (100). All compounds were inseparable by column chromatography.

(c) *With ethylmagnesium bromide (work up with D_2O).* Procedure (a) was repeated except that, after stirring for 30 min at room temperature, D_2O (1 ml) was added. The reaction mixture contained by GLC and GC/MS data 7,7-dibromobicylo[4,1,0]heptane[35] (6%), *7-ethyl-7-deuterio-bicyclo[4,1,0]heptane* (66%, *exo*-**13** (R=Et, E=D)/*endo*-**13**(R=Et, E=D)=3.8:1, R_t (*exo*-**13** (R=Et, E=D)) 3.48 min, (*endo*-**13** (R=Et, E=D)) 4.26 min) which showed (*m/z*, %): 125 (12, M^+), 110 (4), 97 (7), 96 (40), 84 (10), 81 (72), 69 (10), 67 (100), 54 (84); tricyclo-[4.1.0.0^{2,7}]heptane and tricyclo[3.2.0.0^{2,7}]heptane (9%, R_t 2.16 min),7-ethyl-7-bromobicylo[4,1,0]heptane (2%, R_t 7.30 min), with spectral data identical to those above and *7-ethyl-7′-deuterio-(7,7′)-bi(bicyclo-[4,1,0]heptyl)* (12%, R_t 11.13 and 11.32 min) which showed (*m/z*, %) for isomer with R_t 11.13: 219 (2, M^+), 191 (5), 190 (28), 176 (9), 162 (3), 137 (9), 134 (6), 122 (41), 108 (28), 105 (17), 94 (46), 92 (26), 82 (10), 80 (100), 77 (15), 68 (27), 67 (28), 65 (14), 53 (11); (*m/z*, %) for isomer with R_t 11.32: 219 (2, M^+), 191 (3), 190 (29), 176 (10), 162 (3), 150 (6), 137 (11), 123 (12), 122 (24), 108 (54), 106 (19), 105 (9), 95 (68), 93 (18), 92 (41), 81 (100), 79 (49), 77 (22), 67 (50), 65 (9), 55 (59), 53 (28). The components were inseparable by column chromatography.

(d) *With isopropylmagnesium bromide*. 0.8 M Isopropylmagnesium bromide in THF (5.0 ml, 4.0 mmol, 2.00 mol equiv.) was added to a stirred solution of 7,7-dibromobicylo[4,1,0]heptane (508 mg, 2.0 mmol) in dry THF (4 ml) under nitrogen at room temperature. Stirring was continued for 30 min at room temperature when water (1 ml) was added. The reaction mixture contained by GLC and GC/MS tricyclo[4.1.0.0^{2,7}]heptane[33] and tricyclo[3.2.0.0^{2,7}]-heptane[34] (55%, R_t 2.30 and 2.48 min) with spectral data identical to those above, *7-isopropylbicylo[4,1,0]heptane* (23%, *exo*-**13** (R=*i*-Pr, E=H)/*endo*-**13** (R=*i*-Pr, E=H)= 3.9:1, R_t (*exo*-**13** (R=*i*-Pr, E=H)) 5.11 min, (*endo*-**13** (R=*i*-Pr, E=H)) 6.00 min) which shown (*m/z*, %): 138 (11, M^+), 123 (19), 109 (5), 96 (15), 95 (98), 93 (10), 82 (78), 81 (66), 80 (48), 79 (19), 67 (100); 7-bromo-bicyclo-[4,1,0]heptane[27] (6%, *exo*-**16**/*endo*-**16**=1:1.9, R_t (*exo*-**16**) 6.57 min, (*endo*-**16**) 7.30 min) and *7-isopropyl-7-bromobicyclo[4,1,0]heptane* (1%, R_t 9.20 min) which showed (*m/z*, %): 218 (15, M^+, ^{81}Br), 216 (15, M^+, ^{79}Br), 137 (100), 131 (11), 123 (11), 95 (40), 81 (99), 69 (15). All compounds were inseparable by column chromatography.

1.5.6. Synthesis of 1-bromo-2-hexylcyclopropene. 1.0 M ethylmagnesium bromide in THF (3.9 ml, 3.9 mmol, 1.30 mol equiv.) was added to a stirred solution of 1,1,2-tribromo-2-hexylcyclopropane (1.089 g, 3.0 mmol) in dry THF (6 ml) under nitrogen at room temperature for 12 min. Stirring was continued for 30 min at room temperature when water (0.5 ml) was added. The reaction mixture was diluted with petroleum to 50 ml, dried and evaporated to give a yellow liquid (597 mg) which was purified on silica (15 g) eluting with petroleum to give *1-bromo-2-hexylcyclopropene*[36] (491 mg, 2.42 mmol, 81%) as a colourless liquid which showed δ_H: 0.89–0.93 (3H, m), 1.26–1.47 (6H, m), 1.53 (2H, s), 1.54–1.63 (2H, m), 2.44 (2H, t, J=7.0 Hz); δ_C: 14.0+, 17.1−, 22.5−, 25.4−, 26.3−, 28.9−, 31.5−, 92.2, 118.0; IR (cm^{-1}, film): 2958 s, 2929 s, 2879 s, 2858 s, 1033 s.

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