# The Preparation and Lithiation of 1-Halogenocyclopropenes

Mark S. Baird,* Helmi H. Hussain, and William Nethercott
Department of Organic Chemistry, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU

Reaction of a range of 1,1,2-trihalogenocyclopropanes (halogen = bromine, chlorine) with methyl-lithium in ether at -90—$20\,°C$ leads to 1,2-dehalogenation to the corresponding 1-halogenocyclo-propene. The halogenocyclopropenes are readily lithiated by lithium–halogen exchange with a second equivalent of methyl-lithium to give 1-lithiocyclopropenes, which are in turn trapped by electrophiles; an exception to this is compound (**21**; X = Cl), which leads to 3-methylbuta-1,2-dienylidene (**31**) by initial lithium–hydrogen exchange and loss of lithium chloride. The cyclopropenes (**5**; R = Me, X = Br or Cl) and (**21**; X = Br or Cl) decompose even at temperatures around ambient, leading either to enynes (**6**; R = Me) or halogenoalkynes (**18**; X = Br or Cl). A ^{12}C-labelling study indicates that C-1 of the cyclopropene (**21**; X = Cl) becomes C-2 of the alkyne (**18**; X = Cl) on rearrangement.

The reaction of 1,1-dibromocyclopropanes (**1**; X = Br) with methyl-lithium at temperatures above $-100\,°C$ generally leads to high yields of allenes (**2**); these are apparently derived by rearrangement of an intermediate cyclopropylidene (**3**), or a related carbenoid, and in certain cases the carbene can be trapped in alternative intra- or inter-molecular proccesses.[1] The reaction is thought to proceed by an initial lithium–halogen exchange to produce (**1**; X = Li) which then loses lithium bromide to produce the carbene (carbenoid); evidence for the formation of species (**1**; X = Li) is seen in their trapping by electrophiles either at low temperature or when the stability of the lithio bromide is increased by intramolecular interaction, *e.g.* to oxygen.[1] The corresponding dichlorides generally do not react with methyl-lithium in ether, but do lead to cyclo-propylidenes on reaction with butyl-lithium.[2]
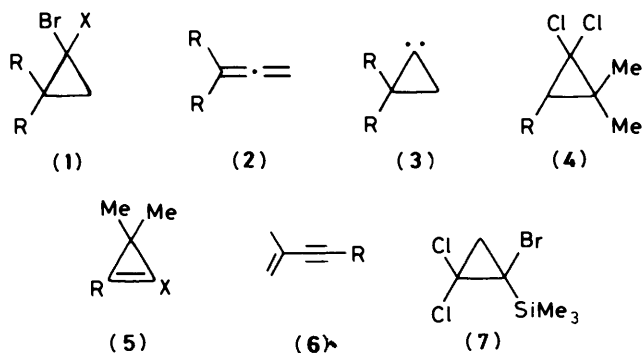
As part of a broad examination of the chemistry of tri- and tetra-halogenated cyclopropanes (halogen = bromine, chlorine)[3] we now report the reactions of a number of 1,1,2-trihalides with methyl-lithium, which do not lead to 1,1-elimination of halogen but instead give 1-halogenocyclopropenes derived from a 1,2-elimination.† 1-Chlorocyclopropenes have previously been obtained by lithiation of cyclopropenes followed by reaction with t-butyl hypochlorite;[4] they have also been postulated as intermediates in the dehydrohalogenation of 1,1-dichlorocyclopropanes and have in certain cases being isolated.[1,5–9]‡ For example reaction of (**4**; R = Bu^t) with potassium t-butoxide in Me$_2$SO leads to compound (**5**; R =

Bu^t, X = Cl), together with (**6**; R = Bu^t).[7] Halogeno- and 1,2-dihalogeno-cyclopropenes have also been obtained by dehalogenosilylation of *e.g.* compound (**7**) with fluoride ion.[10]

Reaction of the chloro dibromide (**8**; X = Cl) with methyl-lithium in ether at $-40\,°C$ followed by quenching with water after 1 min led to the monobromocyclopropene (**9**) in moderate yield (41%). The [1]H n.m.r. spectrum of this product was extremely complex, but the carbon spectrum showed the required nine lines including two singlets in the olefinic region (δ_C 100 and 97.4). Although the cyclopropene decomposed during several hours at 20 °C, it could be trapped by reaction with bromine in carbon tetrachloride to give the tribromide (**8**; X = Br) (45%); moreover, when (**8**; X = Cl) was treated with methyl-lithium in ether at $-40\,°C$ as above and the products were then treated directly with bromine in carbon tetrachloride at that temperature, the tribromide (**8**; X = Br) was obtained in high yield (96%). The formation of (**9**) can be explained in terms of an initial lithium exchange with one of the bromines of the starting material followed by a 1,2-elimination of lithium chloride.

In agreement with this the monocyclic derivative (**10**; R = Bu^t, X = Br) was converted to compound (**11**; R = Bu^t, X = Br) (52%) by reaction with 1 mol equiv. of methyl-lithium under the same conditions. Compound (**11**; R = Bu^t, X = Br) showed a very simple [1]H n.m.r. spectrum including a singlet for the ring hydrogens at δ 1.50, while five peaks were observed in the [13]C n.m.r. spectrum along with two singlets at 124.8 and 89.4 for the alkene carbons; the other ring carbon appeared at δ 16.4. The i.r. spectrum included a double bond stretch at 1 825 cm^{-1}, a position similar to that reported in other 1,2-disubstituted cyclopropenes.[4] Addition of bromine in carbon tetrachloride led to compound (**12**; R = Bu^t, X = Br) in high yield. Although the yield of the bromide (**11**; R = Bu^t, X = Br) was only moderate, this is partly due to difficulties in separating it from the solvent, ether. However, if compound (**10**; R = Bu^t, X = Br) was treated with 2 mol equiv. of methyl-lithium at $-50\,°C$, allowed to reach room temperature for 5 min, and then quenched with propanone or carbon dioxide at $-50\,°C$, the products were (**11**; R = Bu^t, X = CMe$_2$OH) (64%) and (**11**; R = Bu^t, X = CO$_2$H) (78%) respectively.§ Presumably the

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† A preliminary account of some of these results has already appeared: M. S. Baird and W. Nethercott, *Tetrahedron Lett.*, 1983, 605.

‡ Dehydrobromination of 1,1-dibromocyclopropanes to produce 1-bromocyclopropenes is also successful in special cases, see K. Komastu, T. Niwa, H. Akari, and K. Okamoto, *J. Chem. Res.*, 1985, (*S*) 252; (*M*), 2847.

§ Both the acid (**11**; R = Bu^t, X = CO$_2$H) and its methyl ester are relatively reactive towards dimerisation, reacting completely in several hours at 20 °C; the acid dimerised on attempted recrystallisation from dichloromethane and the m.p. reported earlier† is in fact one of the dimers. The related 1,3,3-trimethyl- and 3,3-dimethyl-cyclopropene-carboxylic acids were much more stable, surviving for at least 7 days at $-10\,°C$ in solution in ether.

bromocyclopropene reacts with the excess methyl-lithium to produce compound (11; R = Bu^t, X = Li) which is then trapped by the added electrophile; indeed when (11; R = Bu^t, X = Br) was treated with methyl-lithium at 20 °C and then quenched with carbon dioxide at −50 °C the acid (11; R = Bu^t, X = CO$_2$H) was obtained in high yield. 1-Lithiocyclopropenes have previously been obtained by lithium–hydrogen exchange on cyclopropenes with methyl-lithium in ether, a process which requires several hours at 20 °C (though lithiation using 2-lithio-3-methylbut-2-ene in THF, however, apparently occurs rapidly even at −30 °C [11]).
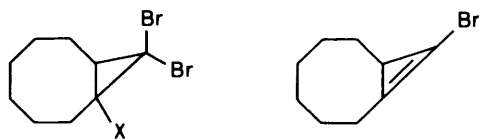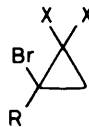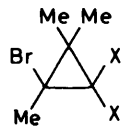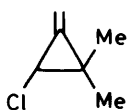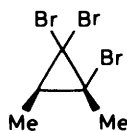

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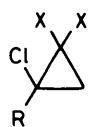
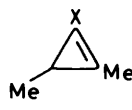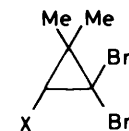(10)   (11)   (12)   (13)

(14)   (15)   (16)   (17)

Treatment of (10; R = Bu^t, X = Cl) with 1 mol. equiv. of methyl-lithium for 25 min at 20 °C also led to a cyclopropene (11; R = Bu^t, X = Cl) (59%). Once again, reaction of the trihalide with 2 equiv. of methyl-lithium led to (11; R = Bu^t, X = Li), though in this case the reaction required 1 h at 20 °C. Trapping with carbon dioxide led to the acid (11; X = CO$_2$H) (72%) (Table 1).

In the same way, treatment of compound (12; R = Bu^i, X = Br), (12; R = Bu^i, X = Cl), (12; R = Oct^n, X = Br), and (12; R = Oct^n, X = Cl) with 1 equiv. of methyl-lithium also produced the corresponding cyclopropenes, (11; R = Bu^i, X = Br), (11; R = Bu^i, X = Cl), (11; R = Oct^n, X = Br), and (11; R = Oct^n, X = Cl) respectively. Compound (11; R = Oct^n, X = Br) was converted to the known cyclopropene (11; R = Oct^n, X = H) [14] by reaction with methyl-lithium at 20 °C, followed by quenching with water, while quenching with D$_2$O led to (11; R = Oct^n, X = D).

Reaction of (13; X = Br, Cl) with methyl-lithium at −40 °C also led to the corresponding halogenocyclopropenes (5; R = Me, X = Br or Cl). The chlorocyclopropene has previously been obtained by halogenation of 1-lithio-2,3,3-trimethylcyclopropene.[4] It is also a likely intermediate in the dehydrohalogenation of (4; R = Me) to (14) and (6; R = Me) on reaction with potassium t-butoxide–Me$_2$SO.[8] The mechanism of alkyne formation in this process was not clear. However, we find that, although compound (5; R = Me, X = Cl) is unchanged (n.m.r.) after standing for 24 h in ether or [^{2}H$_6$]benzene solution, it decomposes when allowed to stand for 18 h at 20 °C in deuteriochloroform to give (6; R = Me); moreover, in Me$_2$SO the cyclopropene is converted to the enyne in 60 min at 20 °C. The bromide (5; R = Me, X = Br) is somewhat less stable, being converted into the same acetylene in

ca. 10 min in deuteriochloroform and 2 min in Me$_2$SO at 20 °C; in this case ^{1}H n.m.r. signals due to the alkyne were also observed when the cyclopropene was allowed to stand for several hours in ether. Although the distilled yields of the two cyclopropenes (5; X = Br or Cl) were again only moderate, a major reason for this was the volatility of the products and the fact that they were unstable to atmospheric pressure distillation. However, examination of the crude reaction mixtures by n.m.r. spectroscopy showed only signals due to ether and cyclopropene. Moreover, when compound (13; X = Br) was treated with 2 equiv. of methyl-lithium followed by quenching with either trimethylsilyl chloride or propanone, good yields of compounds (5; R = Me, X = SiMe$_3$) and (5; R = Me, X = CMe$_2$OH) respectively were obtained (Table 1). The former was also observed when the isolated compound (5; R = Me, X = Br) was treated with 1 equiv. of methyl-lithium followed by trimethylsilyl chloride, and presumably arises by the trapping of compound (5; R = Me, X = Li) by the chlorosilane. Reaction of compound (13; X = Br) with 2 equiv. of methyl-lithium followed by quenching with carbon dioxide led to the corresponding acid (5; R = Me, X = CO$_2$H) (76%); this has previously been obtained by lithium–hydrogen exchange on 1,1,2-trimethylcyclopropane, followed by carboxylation.[4,11]
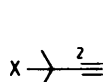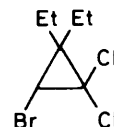
(18)   (19)   (20)   (21)
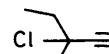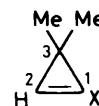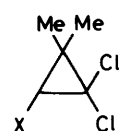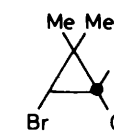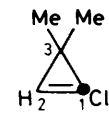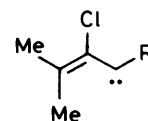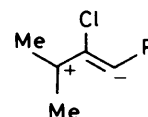
(22)   (23)   (24)   (27)

● = ^{12}C

Treatment of the tribromide (15) with methyl-lithium (1 equiv.) led, as expected, to the cyclopropene (16; X = Br), although the isolated yield was relatively low due to the difficulty in separating the bromide from ether. When compound (15) was treated with 2 equiv. of methyl-lithium followed by quenching with trimethylsilyl chloride a much better yield of the silane (16; X = SiMe$_3$) was obtained. In contrast, treatment of the isomeric tribromide (17; X = Br) or the chloro dibromide (17; X = Cl) with 1 equiv. of methyl-lithium in ether followed by removal of the solvent by distillation at atmospheric pressure led only to the acetylene (18; X = Br). However, if the volatile reaction products and solvent from the first reaction were removed by distillation at 1 mmHg and 20 °C and the ether was then removed from the distillate at −40 °C and 1 mmHg, the only product was the cyclopropene (21; X = Br) which showed just two singlets in the ^{1}H n.m.r. spectrum at δ_H 7.4 (1 H), and 1.2 (6 H). When allowed to stand in chloroform at 20 °C this rearranged to compound (18; X = Br) over a period of ca. 12 h; the reaction appeared to

Table. Preparation of cyclopropenes by reaction of trihalocyclopropanes with methyl-lithium

| Trihalide R	X	MeLi (mol equiv.)	Trapping agent	Cyclopropene R	X	%
(10) Bu^t	Br	1		(11) Bu^t	Br	52
Bu^t	Cl	1		(11) Bu^t	Cl	59
Bu^t	Br	2	CO$_2$	(11) Bu^t	CO$_2$H	78
Bu^t	Cl	2	CO$_2$	(11) Bu^t	CO$_2$H	72
Bu^t	Br	2	Me$_2$CO	(11) Bu^t	CMe$_2$OH	64
(12) Oct^n	Cl	1		(11) Oct^n	Cl	94
Oct^n	Br	1		(11) Oct^n	Br	56
Bu^i	Br	1		(11) Bu^i	Br	57
Bu^i	Cl	1		(11) Bu^i	Cl	57
(13)	Br	1		(5) Me	Br	43
	Cl	1		(5) Me	Cl	38
	Br	2	Me$_3$SiCl	(5) Me	SiMe$_3$	71
	Br	2	CO$_2$	(5) Me	CO$_2$H	76
	Br	2	Me$_2$CO	(5) Me	CMe$_2$OH	75
	Cl	2	Me$_2$CO	(5) Me	CMe$_2$OH	63
(17)	Br	1		(21)	Br	31
	Br	2	Me$_3$SiCl	(21)	SiMe$_3$	77
(15)	Br	1		(16)	Br	31
	Cl	2	Me$_3$SiCl	(16)	SiMe$_3$	61
	Br	2	Me$_3$SiCl	(16)	SiMe$_3$	71
(17)	Cl	1		(21)	Cl	a
(17)	Cl	2	ClCO$_2$Me	(21)	CO$_2$Me	70

^{a} Only product by ^{13}C or ^{1}H n.m.r. spectroscopy but too volatile/unstable to separate completely from ether.

(26)   (28)   (29)   (30)

(31)   (25)   ● = ^{12}C

increase in rate as the amount of residual ether in the sample was reduced. This cyclopropene is therefore much more stable than previously suggested.* Reaction of the corresponding bromo dichloride (22; X = Br) with methyl-lithium at −78 °C gave a single volatile product which could not be separated completely from ether by vacuum distillation. The proton n.m.r. spectrum of the ethereal solution showed a single hydrogen resonance at δ_H 7.4 together with a single at δ_H 1.2 (6 H), and on this basis the compound is assigned the structure (21; X = Cl). The ^{13}C n.m.r. spectrum of the solution showed just four signals in addition to those for ether—two in the alkene region and two at higher field—in complete agreement with the cyclopropene structure. The initial reactions of the three trihalides (17; X = Br or Cl) and (22; X = Br) therefore all involved a 1,2-dehalogenation initiated by a lithium–halogen exchange, even though a cyclopropane hydrogen was also available for lithium–hydrogen exchange; it is interesting therefore to note that the trichloride (22; X = Cl) reacts with methyl-lithium by dehydrohalogenation initiated by lithium–hydrogen exchange.[12] If the sample of compound (21; X = Cl) was diluted with chloroform and allowed to stand at 20 °C, a rearrangement took place over a period of 10 days in which the n.m.r. signals due to cyclopropene were replaced by those due to (18; X = Cl).† In the same way compound (19) was converted into (20) by reaction with methyl-lithium followed by removal of the solvent at atmospheric pressure.

In order to probe the mechanism of these conversions, the labelled cyclopropane (23) was prepared by reaction of ^{12}CHCl$_3$–aqueous NaOH–TEBA with 1-bromo-2-methylprop-
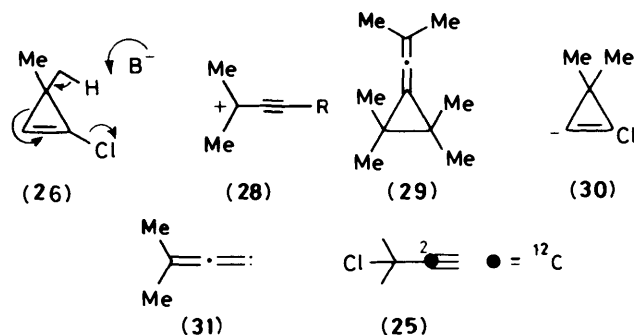
1-ene in dichloromethane. Treatment of compound (23) with methyl-lithium (1 equiv.) and quenching with water led to an ethereal solution of the cyclopropene (24), the ^{13}C n.m.r. spectrum of which was identical to that of the unlabelled sample (21; X = Cl), apart from the absence of the signal due to the quaternary alkene carbon at δ_C 129.5. After 10 days as above this rearranged to 3-chloro-3-methylbutyne (18; X = Cl) in which there was no signal for C-2 in the carbon spectrum, i.e. the product is (25) and the 2,3-bond of the cyclopropene is broken in the ring-opening process. When either (21; X = Br) or (21; X = Cl) was dissolved in [^{2}H$_6$]Me$_2$SO, the signals due to the starting material disappeared over a period of ca. 10 min at 20 °C and were replaced by those due to 3-methylbut-3-en-1-yne. It is interesting to note that (21; X = Cl) has been proposed as an intermediate in the formation of this acetylene as one product of the dehydrohalogenation of 1,1-dichloro-2,2-dimethylcyclopropane by potassium t-butoxide in HMPA, and that the mechanism shown in (26) has been put forward;[6] in the light of the instability of compound (21; X = Cl), the transformation may well not require the strong base. In view of the known ring opening of 1,2-dihalogeno-3,3-dimethylcyclopropenes to vinylcarbenes at temperatures around ambient,[12] it is possible that the formation of alkynes (18; X = Br or Cl) from cyclopropenes (21; X = Br or Cl) occurs by a similar ring opening to (27; R = H), followed by a [1,2]-shift of halogen. However, the effect of different solvents on the rate of ring opening of (21; X = Br or Cl) and (5; R = Me, X = Br or Cl) and the fact that dehydrohalogenations occur in Me$_2$SO suggests reactions involving the formation of the ion (28; R = H or Me), which can either be trapped by the halide counter ion or eliminate a proton in a basic solvent.

Reaction of compound (17; X = Br) with 2 mol equiv. of methyl-lithium followed by quenching with carbon dioxide led to the acid (21; X = CO$_2$H) (71%). Similarly reaction of (17; X = Cl) with 2 equiv. of methyl-lithium followed by quenching with methyl chloroformate or trimethylsilyl chloride led to (21; X = CO$_2$Me) and (21; X = SiMe$_3$) respectively. In each case the product is again derived by lithium–bromine exchange in the intermediate cyclopropene (21; X = Br) and trapping of the derived lithiocyclopropene (21; X = Li).‡ However, the reaction of (22; X = Br) with 2 equiv. of methyl-lithium followed by quenching with chlorotrimethylsilane gave a complex product showing no alkene signal corresponding to the silyl ether (21; X = SiMe$_3$) and, when excess 2,3-dimethylbut-2-ene was present during the reaction, the allene (29) was obtained as the major product. This suggests that the intermediate in this case, the chlorocyclopropene (21; X = Cl), undergoes lithium–hydrogen exchange with methyl-lithium faster than lithium–chlorine exchange; the anion (30) (or a lithio derivative) then

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* A preliminary account of some of these results has already appeared: M. S. Baird and W. Nethercott, *Tetrahedron Lett.*, 1983, 605.

† Identical with those for an authentic sample.[21] Compound (18; X = Cl) has been postulated as an intermediate in a rearrangement leading to (18; X = OEt), see D. Seyferth and T. F. Jula, *J. Organomet. Chem.*, 1968, **14**, 109. A related rearrangement has been reported for 1-fluorocyclopropenes, obtained by reaction of 1,1-difluorocyclopropanes with butyl-lithium, see M. Suda, *Tetrahedron Lett.*, 1980, 4355.

‡ 1-Trimethylsilylcyclopropenes have recently been obtained in several steps from 3-trimethylsilylprop-2-yn-1-ols, but the method is not successful unless there is a substituent at the 2-position of the cyclopropene, see A. T. Stoll and E. Negishi, *Tetrahedron Lett.*, 1985, 5671.

undergoes rapid loss of halide ion to give the carbene (31), which is trapped by the alkene.

The above results show that, in general, whatever combination of bromine and chlorine is used in compounds (10), (12), (13), or (22), reaction with 1 equiv. of methyl-lithium leads to 1,2-dehalogenation to a 1-halogenocyclopropene; the only exception occurs with 1,1,2-trichlorocyclopropanes having a hydrogen at the 2-position *i.e.* (22; X = Cl), when dehydrohalogenation occurs.[12] In the case of the other trichlorides, the dehalogenation reaction requires several minutes at 20 °C to proceed to completion, whereas the 1,1,2-tribromides and 1,1-dibromo-2-chlorides react in 2 min even at −90 °C. The fact that the trichlorides react even at 20 °C is in contrast to 1,1-dichlorocyclopropanes which generally do not react with methyl-lithium in ether, and presumably reflects the effect of the third halogen on the rate of lithium–chlorine exchange at the 1-position. 2-Bromo-1,1-dichlorides react in *ca.* 2 min at 0 °C. It is not clear whether this occurs by initial lithium–chlorine or lithium–bromine exchange, but the fact that the reaction occurs rapidly even at 0 °C suggests that the latter might be correct, as lithium–chlorine exchange in 1,1,2-trichlorides is rather slower (see above). The 1-bromocyclopropenes (11; R = alkyl, X = Br), (5; R = Me, X = Br) and (21; X = Br) react with methyl-lithium in a few minutes at −40 °C by lithium–bromine exchange, while the chlorocyclopropenes (11; R = alkyl, X = Cl) and (5; R = Me, X = Cl) react by lithium–chlorine exchange in *ca.* 1 h at 20 °C; in contrast, when a 2-hydrogen is present in the 1-chlorocyclopropene the reaction follows a different course, apparently initiated by lithium–hydrogen exchange.

Experimental

Magnesium sulphate was used throughout for drying organic extracts. Reactions involving the addition of methyl-lithium were carried out under an atmosphere of nitrogen unless otherwise stated.

Capillary g.l.c. was carried out using a 40M SE30 column. Infrared spectra were obtained as KBr discs (solids) or as liquid films on Perkin-Elmer 257 or Nicolet instruments, while n.m.r. spectroscopy was carried out in $CDCl_3$ solution (unless otherwise stated) on Varian EM 360 (proton) or Bruker WM300 spectrometers (proton and carbon). Mass spectra were obtained using AEI MS9 or Kratos MS80 instruments.

Except where otherwise stated, trihalocyclopropanes were prepared as previously described.[13] All new compounds were homogeneous by t.l.c. [SiO_2; light petroleum (b.p. 40—60 °C)] and/or g.l.c.

1,1,3-Tribromo-2,2,3-trimethylcyclopropane (13; X = Br).— Sodium hydroxide (10 g) in water (10 ml) was added to a rapidly stirred solution of 2-bromo-3-methylbut-2-ene (5.0 g) and cetrimide (0.5 g) in bromoform (50 ml). After 3 h at 65 °C the products were extracted with dichloromethane (3 × 20 ml) and the combined organic layers were dried and the solvent was removed at 14 mmHg to give a solid. Recrystallisation from ethanol gave *1,1,3-tribromo-2,2,3-trimethylcyclopropane* (7.3 g, 68%), m.p. 93—94 °C (Found: C, 22.3; H, 2.7%; M^+, 238.9094. $C_6H_9Br_3$ requires C, 22.43; H, 2.80%; M, 238.9072) which showed δ_H 1.98 (3 H, s), 1.50 (3 H, s), and 1.36 (3 H, s); δ_C 51.7 (s), 51.0 (s), 33.0 (s), 26.6 (q), and 20.8 (q); $\nu_{max.}$ 775vs cm^{-1}.

3-Bromo-1,1-dichloro-2,2,3-trimethylcyclopropane (13; X = Cl).—Sodium hydroxide (10 g) in water (10 ml) was added over 15 min to a rapidly stirred solution of 2-bromo-3-methylbut-2-ene (5.0 g) and cetrimide (0.5 g) in chloroform (50 ml). After 2 h at 20 °C the products were extracted with water (3 × 20 ml) and worked up as before to give 3-bromo-2,2-dichloro-1,1,3-

trimethylcyclopropane (5.1 g, 64%), m.p. 62—63 °C (Found: C, 30.9; H, 3.8. $C_6H_9BrCl_2$ requires C, 31.03; H, 3.88%) which showed δ_H 1.90 (3 H, s), 1.42 (3 H, s), and 1.30 (3 H, s); δ_C 73.3 (s), 50.3 (s), 33.1 (s), 24.5 (q), 24.1 (q), and 18.4 (q); $\nu_{max.}$ 870s, 815s, and 710m cm^{-1}

2-Bromo-1,1-dichloro-2-isobutylcyclopropane (12; R = Bu^i, X = Cl).—Sodium hydroxide (6.0 g) in water (6 ml) was added over 1 min to a stirred solution of 2-bromo-4-methylpent-1-ene[15] (5.0 g) and cetrimide (50 mg) in chloroform (10 ml). After the reaction had been refluxed for 4 h, the products were worked up as above and the residue was purified by column chromatography over silica, eluting with light petroleum, b.p. 40—60 °C, and characterised as *2-bromo-2-isobutyl-1,1-dichlorocyclopropane* (6.7 g, 89%) (Found: C, 34.4; H, 4.3. $C_7H_{11}BrCl_2$ requires C, 34.2; H, 4.5%) which showed δ_H 1.4—2.4 (3 H, m) and 0.7—1.35 (8 H, m); $\nu_{max.}$ 1 480s, 1 045s, and 775s cm^{-1}.

1,1,2-Tribromo-2-isobutylcyclopropane (12; R = Bu^i, X = Br).—The above reaction was repeated using bromoform (5 ml) in place of chloroform. After 2 h at 60 °C work-up as above gave 1,1,2-*tribromo-2-isobutylcyclopropane* (6.5 g, 79%) which was one spot on t.l.c. (Found: M^+, 333.8395. $C_7H_{11}$$^{79}Br^{81}Br$ requires M, 333.8391) and showed δ_H 1.5—2.7 (5 H, m) and 1.05 (6 H, br t); δ_C 48.5 (t), 44.8 (s), 38.3 (t), 33.3 (s), 28.7 (d), 22.5 (q), and 21.4 (q); $\nu_{max.}$ 1 475s and 1 030s cm^{-1}.

3-Bromo-1,1-dichloro-2,2-diethylcyclopropane (19).—Sodium hydroxide (30 g) in water (30 ml) was added over 1 min to a rapidly stirred solution of 1-bromo-2-ethylbut-1-ene (15 g) and cetrimide (0.4 g) in chloroform (50 ml). A vigorous exothermic reaction occurred and the solvent refluxed. The products were heated under reflux for 160 min and then water (160 ml) was added. The aqueous layer was extracted with chloroform (3 × 100 ml) and the combined organic layers were washed with brine (3 × 300 ml), dried, and the solvent removed at 14 mmHg. The crude product was purified by column chromatography over silica, eluting with light petroleum (b.p. 40—60 °C) and then distilled to give 3-*bromo-1,1-dichloro-2,2-diethylcyclopropane* (16.4 g, 73%), b.p. 39—45 °C at 0.01 mmHg (Found: C, 34.15; H, 4.35. $C_7H_{11}BrCl_2$ requires C, 34.18; H, 4.51%) which showed δ_H 3.23 (1 H, s), 1.70 (4 H, q, J 7.5 Hz, further split), 1.03 (3 H, t, J 7.5 Hz), and 0.99 (3 H, t, J 7.5 Hz); δ_C 68.9, 40.7, 38.7, 25.7, 23.1, 10.1, and 9.4; $\nu_{max.}$ 1 465s and 860s cm^{-1}.

9-Bromobicyclo[6.1.0]*non-9-ene* (9).—Methyl-lithium (2.6 ml; 1.5M) was added over 2 min to a stirred solution of 9,9-dibromo-1-chlorobicyclo[6.1.0]nonane (1.0 g) in ether (30 ml) at −40 °C. After 1 min the products were quenched carefully with water (1 ml, then 20 ml). The aqueous layer was washed with ether (3 × 30 ml), the combined organic layers were dried, and the solvent was removed at 14 mmHg. The resulting oil was one major spot on t.l.c.; purification by column chromatography over basic alumina, eluting with light petroleum (b.p. 40—60 °C) gave 9-*bromobicyclo*[6.1.0]*non-9-ene* (260 mg, 41%) (Found: M^+, 200.0191. $C_9H_{13}Br$ requires M, 200.0201) which showed δ_H 2.0—3.1 (m) and 1.2—2.0 (m); δ_C 100.0, 97.4, 30.6, 29.5, 29.3, 27.7, 26.6, 25.1, and 24.8; $\nu_{max.}$ 2 920s, 2 870m, and 1 710m cm^{-1}.

1,9,9-Tribromobicyclo[6.1.0]*nonane* (8; X = Br).—(*a*) A dilute solution of bromine in ether was added to 9-bromobicyclo[6.1.0]non-9-ene (37 mg) in ether (10 ml) at 20 °C until a faint red colour persisted. Removal of the solvent gave a dark oil (96 mg) which was purified by column chromatography on silica, eluting with light petroleum (b.p. 40—60 °C), to give an oil which was one spot on t.l.c., characterised as 1,9,9-*tribromobicyclo*[6.1.0]*nonane* (30 mg, 45%) (Found: M^+,

357.8563. $C_9H_{13}Br_3$ requires M, 357.8567) which showed δ_H 0.8—3.1 (complex); v_{max}. 2 900s, 2 850s, 1 465s, and 1 450s cm^{-1}.

(b) Methyl-lithium (0.2 ml; 1.5M) was added to a stirred solution of 9,9-dibromo-1-chlorobicyclo[6.1.0]nonane (100 mg) in ether (2 ml) at −40 °C. After 5 min water (0.1 ml) was added, followed by an excess of a dilute solution of bromine in carbon tetrachloride at −40 °C; the reaction was allowed to reach 20 °C, worked up, dried, and the solvent was removed at 14 mmHg to give an oil (110 mg, 96%) which was one spot on t.l.c. and was identical by m.s. and n.m.r. spectroscopy to the tribromide obtained in (a).

1-*Bromo*-2-t-*butylcyclopropene* (11; R = Bu^t, X = Br).— Methyl-lithium (15 ml; 1.5M) was added over 10 min to a stirred solution of 1,1-dibromo-2-chloro-2-t-butylcyclopropane (5.0 g) in ether (70 ml) at −40 to −50 °C. The products were quenched by the careful addition of water (5 ml) at that temperature and allowed to reach ambient temperature. The aqueous layer was washed with ether (2 × 20 ml) and the combined organic layers were dried. The bulk of the ether was removed by distillation through a Vigreux column at 760 mmHg, and final traces were separated by distillation at 14 mmHg which gave 1-*bromo*-2-t-*butylcyclopropene* (1.55 g, 51.5%), b.p. 31—32 °C at 14 mmHg (Found: M^+, 174.0058. $C_7H_{11}Br$ requires M, 174.0044) which showed δ_H 1.50 (2 H, s) and 1.20 (9 H, s); δ_C 124.8 (s), 89.4 (s), 31.1 (s), 27.2 (q), and 16.4 (t); v_{max}. 2 930s, 1 825m, 1 485s, and 970s cm^{-1}.

Bromination of 1-*Bromo*-2-t-*butylcyclopropene*.—Bromine in carbon tetrachloride (10% v/v) was added dropwise at 20 °C to a stirred solution of 1-bromo-2-t-butylcyclopropene (100 mg) in carbon tetrachloride (0.5 ml) until a faint red colour persisted. Removal of the solvent at 14 mmHg gave an oil (178 mg, 94%) which was one peak on capillary g.l.c. and was characterised as 1,1,2-*tribromo*-2-t-*butylcyclopropane* (12; R = Bu^t, X = Br) (Found: M^+, 333.8395. $C_7H_{11}{}^{79}Br_2{}^{81}Br$ requires M, 333.8391) which showed δ_H 2.18 (1 H, d, J 9 Hz), 1.83 (1 H, d, J 9 Hz), and 1.31 (9 H, s); v_{max}. 1 490s, 1 470s, and 1 000s cm^{-1}.

2-(t-*Butylcyclopropen*-1-*yl*)*propan*-2-*ol* (11; R = Bu^t, X = Me$_2$COH).—Methyl-lithium (11 ml; 1.55M) was added over 5 min to a stirred solution of 1,1-dibromo-2-chloro-2-t-butyl-cyclopropane (2.0 g) in ether (15 ml) at −78 °C. The products were allowed to reach 20 °C for 5 min and were then cooled to −50 °C and treated with acetone (1.0 ml) and again allowed to reach 20 °C. Work-up as before and removal of the solvent at 14 mmHg gave an oil which was distilled to give 2-(t-*butylcyclo-propen*-1-*yl*)*propan*-2-*ol*, b.p. 45 °C at 2 mmHg (0.85 g, 64%) (Found: M^+, 153.1268. $C_{10}H_{17}O$ requires M, 153.1279) which gave a single peak on g.l.c. and showed δ_H 1.89 (1 H, br s, OH), 1.43 (6 H, s), 1.15 (9 H, s), and 0.89 (2 H, s); v_{max}. 3 390s, 1 880m, 1 362s, 1 166br, and 947m cm^{-1}.

1-*Chloro*-2-t-*butylcyclopropene* (11; R = Bu^t, X = Cl).— Methyl-lithium (40 ml; 1.5M) was added over 10 min to a stirred solution of 1,1,2-trichloro-2-t-butylcyclopropane (5.0 g) in ether (70 ml) at −40 °C. Work-up of a portion by quenching with water and analysis by g.l.c. showed no reaction to have occurred. The temperature was allowed to reach ambient, when a heavy precipitate formed. After 25 min the products were worked up as above; distillation of the residue gave 1-*chloro*-2-t-*butylcyclopropene* (0.9 g, 59%), as a colourless liquid, b.p. 21—22 °C at 14 mmHg (Found: M^+, 130.0547. $C_7H_{11}Cl$ requires M, 130.0549) which showed δ_H 1.50 (2 H, s) and 1.19 (9 H, s); δ_C 118.0 (s), 103.7 (s), 30.9 (s), 27.4 (q), and 15.8 (t); v_{max}. 1 835w, 1 375s, 1 040s, and 985s cm^{-1}.

2-t-*Butylcyclopropene*-1-*carboxylic Acid* (11; R = Bu^t, X = CO$_2$H).—(a) Methyl-lithium (2.5 ml; 1.55M) was added at −78 °C to a stirred solution of 1,1-dibromo-2-chloro-2-t-butylcyclopropane (0.45 g) in ether (10 ml). The products were allowed to reach 20 °C and were then cooled to −50 °C. Gaseous carbon dioxide was passed through the products for 15 min, and the temperature was then allowed to reach 20 °C while the gas stream was maintained. Water (10 ml) was added at −20 °C and the products were then acidified with hydrochloric acid (5 ml; 10%) and extracted with ether (2 × 10 ml). The combined ether layers were dried and the solvent was removed at 14 mmHg to give 2-t-*butylcyclopropene*-1-*carboxylic acid* (0.17 g, 78%) as a pale yellow solid which showed δ_H 8.35 (1 H, br s, OH), 1.40 (2 H, s), and 1.26 (9 H, s); this underwent a rapid dimerisation on attempted recrystallisation, the products of which will be described elsewhere. However, reaction with one equivalent of diazomethane in ether at −30 °C gave the corresponding methyl ester (86%) (Found: M^+, 154.0938. $C_9H_{14}O_2$ requires M, 154.0994).

(b) 1-Bromo-2-t-butylcyclopropene (300 mg) in ether (1 ml) was treated with methyl-lithium (1 ml; 2M). After 5 min the products were cooled to −40 °C and a rapid stream of carbon dioxide was passed through the solution for 20 min. The temperature was allowed to reach 0 °C and was then reduced again to −40 °C. Water (0.25 ml) was added, followed by sulphuric acid (0.25 ml; 25% v/v). The aqueous layer was extracted with ether (5 ml), and the combined organic layers were washed with water (2 × 1 ml), dried, and evaporated at 14 mmHg. A pale yellow solid was obtained which was identical by n.m.r. spectroscopy to the above acid (218 mg, 91%).

(c) Methyl-lithium (16.0 ml, 1.55M) was added as above to 1,1,2-trichloro-2-t-butylcyclopropane (2.0 g) in ether 20 ml at 0 °C. The products were allowed to reach 20 °C; after 60 min they were cooled to −50 °C and treated with carbon dioxide as above. Work-up gave compound (11; R = Bu^t, X = CO$_2$Me) (1.0 g, 72%) as a pale yellow solid, identical by n.m.r. spectroscopy to that above.

1-*Bromo*-2-*isobutylcyclopropene* (11; R = Bu^i, X = Br).— Methyl-lithium (10 ml; 2M) was added over 3 min to a stirred solution of 1,1,2-tribromo-2-isobutylcyclopropane (5.0 g) in ether (40 ml) at −40 to −50 °C. After 5 min the products were worked up as before and the bulk of the solvent was removed at 760 mmHg; distillation of the residue at 45—46 °C at 20 mmHg gave 1-*bromo*-2-*isobutylcyclopropene* (1.49 g, 57%) (Found: M^+, 174.0049. $C_7H_{11}Br$ requires M, 174.0044) which showed δ_H 2.33 (2 H, dd, J 7, 1.5 Hz), 1.5—2.3 (1 H, m), 1.50 (2 H, s), and 1.00 (6 H, d, J 7 Hz); v_{max}. 1 835m, 1 480s, and 1 045s cm^{-1}.

A residue remained after the distillation (580 mg) which was apparently a complex mixture (n.m.r.).

1-*Chloro*-2-*isobutylcyclopropene* (11; R = Bu^i, X = Cl).— Methyl-lithium (11 ml; 2.27M) was added over 5 min at −40 to −50 °C to a stirred solution of 2-bromo-1,1-dichloro-2-isobutylcyclopropane (5.0 g) in ether (40 ml). After 5 min, water (5 ml) was added carefully at that temperature and the products were allowed to reach ambient temperature. Work-up as before and removal of the solvent at 760 mmHg gave an oil which was distilled to produce 1-*chloro*-2-*isobutylcyclopropene* (1.52 g, 57%), b.p. 33 °C at 20 mmHg (Found: M^+, 130.0543. $C_7H_{11}Cl$ requires M, 130.0549) which showed δ_H 2.37 (2 H, d), 1.9 (1 H, m), 1.50 (2 H, s), and 0.98 (6 H, d, J 6 Hz); v_{max}. 1 840m and 1 040s cm^{-1}.

A residue remained after the distillation (560 mg) which appeared to be a complex mixture on the basis of n.m.r. spectroscopy.

1,1,2-*Tribromo*-2-*octylcyclopropane* (12; R = n-C$_8$H$_{17}$, X =

Br).—Sodium hydroxide (15 g) in water (15 ml) was added in one portion to a rapidly stirred mixture of 2-bromodec-1-ene[20] (8.0 g), cetrimide (0.3 g) and bromoform (30 g). A vigorous reaction occurred and the temperature was kept just below 70 °C by external cooling. The products were then heated for 1 h at 70 °C and worked up as before. The product was purified by chromatography on silica eluting with light petroleum (b.p. 40—60 °C) and identified as 1,1,2-*tribromo-2-octylcyclopropane* (8.7 g, 61%) (Found: C, 33.7; H, 4.5. $C_{11}H_9Br_3$ requires C, 33.8; H, 4.9%) which showed δ_H 1.65—2.4 (m), 1.1—1.5 (m), and 0.6—1.1 (m).

2-*Bromo*-1,1-*dichloro-2-octylcyclopropane* (12; R = n-C_8H_{17}, X = Cl).—Sodium hydroxide (6.0 g) in water (6 ml) was added in one portion to a rapidly stirred mixture of 2-bromodec-1-ene (2.9 g) and cetrimide (50 mg) in chloroform (10 ml). After refluxing for 4 h the products were worked up as before to give, after chromatography on silica eluting with light petroleum, b.p. 40—60 °C, 2-*bromo*-1,1-*dichloro-2-octylcyclopropane* (2.3 g, 58%) (Found: C, 44.2; H, 6.2. $C_{11}H_{19}BrCl_2$ requires C, 43.9; H, 6.4%) which showed δ_H 1.7—2.1 (3 H, m), 1.1—1.65 (13 H, m), and 0.7—1.1 (3 H, m); $v_{max.}$ 770s cm^{-1}.

1-*Chloro-2-octylcyclopropene* (11; R = n-C_8H_{17}, X = Cl).— Methyl-lithium (1.4 ml; 1.5M) was added over 1 min to 2-bromo-1,1-dichloro-2-octylcyclopropane (500 mg) in ether (10 ml) at 20 °C. After 2 min the products were quenched with water and worked up as before, removing the solvent at 14 mmHg. A colourless oil remained which was one spot on t.l.c. and was characterised as 1-*chloro-2-octylcyclopropene* (290 mg, 94%) which showed δ_H 1.6—2.1 (m), 1.1—1.6 (m), 0.7—1.1 (m); m/z 151 (M^+ − Cl),129/131 (3:1, M^+ − Bu).

1-*Bromo-2-octylcyclopropene* (11; R = n-C_8H_{17}, X = Br).— Methyl-lithium (10.2 ml; 1.5M) was added over 5 min to 1,1,2-tribromo-2-octylcyclopropane (5.0 g) in ether (50 ml) at 20 °C. After the reaction had been stirred for 5 min, the products were worked up as above and the solvent was removed at 14 mmHg. The remaining oil showed one major and two minor spots in t.l.c. and the major component was obtained as a colourless oil by chromatography on basic alumina, eluting with light petroleum, m.p. 40—60 °C, and characterised as 1-*bromo-2-octylcyclopropene* (1.64 g, 56%) which showed δ_H 2.42 (2 H, br t, 6 Hz), 0.7—1.9 (15 H, m), and 1.50 (2 H, s); δ_C 118.1, 92.3, 31.8, 29.3, 26.4, 25.5, 22.7, 17.2, and 14.1; m/z 173/175 (1:1, M^+ − C_4H_9), 159/161 (1:1, M^+ − C_5H_{11}), 151 (M^+ − Br). This compound was characterised by conversion to 1-octylcyclopropene (see below).

1-*Octylcyclopropene* (11; R = n-C_8H_{17}, X = H).—(a) Butyl-lithium (0.9 ml; 1.5M) was added over 1 min to a stirred solution of 1-bromo-2-octylcyclopropene (300 mg) in ether (8 ml) under argon at 20 °C. After 15 min, water (1 ml) was added. The organic layer was dried and the solvent was removed at 14 mmHg. The remaining oil was one spot on t.l.c., and was identified as 1-octylcyclopropene (Found: M^+, 152.1564. Calc. for $C_{11}H_{20}$: M, 152.1565) which showed a ^1H n.m.r. spectrum identical to that reported,[14] and included a signal at 97.8 (d) in the ^{13}C spectrum.

(b) Methyl-lithium (0.9 ml; 1.5M) was added over 1 min at 20 °C to 1,1,2-tribromo-2-octylcyclopropane (200 mg) in ether (4 ml). After 7 h at 20 °C work-up as above gave an oil which was one spot on t.l.c. and was characterised as 1-octylcyclopropene.

2-*Deuterio*-1-*octylcyclopropene* (11; R = n-C_8H_{17}, X = D).—Butyl-lithium (0.3 ml; 1.55M) was added over 1 min to 1-bromo-2-octylcyclopropene (100 mg) in ether (5 ml) at 20 °C.

After 15 min, D_2O (0.5 ml) was added. Work-up as above led to an oil which showed a single major spot on t.l.c. and was characterised as 2-*deuterio*-1-*octylcyclopropene* (74 mg, 95%) (Found: M^+, 153.1633. $C_{11}H_{19}D$ requires M, 153.1628) which showed δ_H 2.46 (2 H, t, J 6 Hz) and 0.7—2.2 (17 H, complex multiplet).

1-*Chloro*-2,3,3-*trimethylcyclopropene* (5; R = Me, X = Cl). —Methyl-lithium (6.2 ml; 1.55M) was added over 2 min to a stirred solution of 3-bromo-2,2-dichloro-1,1,3-trimethylcyclo-propane (2.0 g) in ether (15 ml) at −40 to −50 °C. The products were allowed to reach room temperature and after 10 min were cooled to −40 °C and quenched by careful addition of water (2 ml). The aqueous layer was extracted with ether (2 × 10 ml) and the combined organic layers were dried and the solvent removed at 14 mmHg and −40 °C. A small amount of the product co-distilled with the ether but the bulk was obtained by distillation of the residue at 20 °C and 1 mmHg and characterised as 1-*chloro*-2,3,3-*trimethylcyclopropene* (0.38 g, 38%) (Found: M^+, 116.0404. C_6H_9Cl requires M, 116.0393) which showed δ_H 1.95 (3 H, s) and 1.18 (6 H, s); $v_{max.}$ 1 840s, 1 370s, and 795s cm^{-1}.

Decomposition of 1-*Chloro*-2,3,3-*trimethylcyclopropene.*—(a) *In chloroform.* The chlorocyclopropene was allowed to stand for 18 h in solution in $CDCl_3$ when complete reaction had occurred. G.l.c. showed the formation of one major component which was collected and characterised as 2-methylpent-1-en-3-yne (6; R = Me) which showed δ_H 5.19 (1 H, br s), 5.14 (1 H, br s), 1.94 (3 H, s), and 1.86 (3 H, s); $v_{max.}$ 3 097 (m), 223.4 (m), 1 615 (s), and 893 (s) cm^{-1}.

(b) *In chloroform–furan.* An n.m.r. sample of the chlorocyclo-propene in $CDCl_3$ was treated with *ca.* 1 mol equiv. of furan and allowed to stand for 18 h. At the end of this time, g.l.c. showed complete consumption of the starting material and the formation of 2-methylpent-1-en-3-yne but there was no evidence for any trapping products derived from the furan.

Reaction of 1,1,3-*Tribromo*-2,2,3-*trimethylcyclopropane with Methyl-lithium.*—Methyl-lithium (4.5 ml; 1.55M) was added over 2 min to a stirred solution of the tribromide (2.0 g) in ether (10 ml) at −78 °C. After 5 min the volatile products were distilled at 20 °C and 1 mmHg and the ether was then removed from the distillate at −40 °C and 1 mmHg to leave an oil which was characterised as 1-*bromo*-2,3,3-*trimethylcyclopropene* (5; R = Me, X = Br) (0.43 g, 43%) (Found: M^+, 159.9893. C_6H_9Br requires M, 159.9877) which showed δ_H 2.0 (3 H, s) and 1.15 (6 H, s); $v_{max.}$ 1 822m, 1 365m, and 785m cm^{-1}.

Decomposition of 1-*Bromo*-2,3,3-*trimethylcyclopropene.*—(a) The bromide (30 mg) was dissolved in [$^2H_6$]Me_2SO (0.5 ml) and the reaction was monitored by n.m.r. spectroscopy. After *ca.* 2 min the ^1H n.m.r. signals due to starting material had completely disappeared and been replaced by three new lines. The products were allowed to stand for 45 min at 20 °C and were then separated by distillation at 20 °C and 1 mmHg and characterised as 2-methylpent-1-en-3-yne (8 mg, 53%) which gave n.m.r. and mass spectra identical to an authentic sample.

(b) A solution of the bromide in deuteriochloroform was monitored by n.m.r. spectroscopy. After 10 min the signals for starting material had been replaced by those due to 2-methyl-pent-1-en-3-yne.

1,3,3-*Trimethyl*-2-*trimethylsilylcyclopropene* (5; R = Me, X = SiMe₃).—Methyl-lithium (9 ml; 1.55M) was added over 2 min to 1,1,3-tribromo-2,2,3-trimethylcyclopropane (2.0 g) in ether (20 ml) at −50 °C under nitrogen. The products were allowed to reach ambient temperature. After 10 min the

temperature was reduced to -50 °C and trimethylsilyl chloride (1.0 g) was added dropwise. The products were again allowed to reach ambient temperature and were then treated with water (1 ml). The ethereal layer was washed with water (3 × 30 ml), dried, and the solvent was removed at 14 mmHg. The residue was flash distilled at 20 °C and 1 mmHg to give 1,3,3-*trimethyl-2-trimethylsilylcyclopropene* (0.69 g, 71%) (Found: M^+, 154.1190. $C_9H_{18}Si$ requires M, 154.1178) which showed δ_H 1.85 (3 H, s), 1.0 (6 H, s), and 0.1 (9 H, s); δ_C 128.7 (s), 119.4 (s), 70.8 (s), 29.3 (q), 21.7 (s), and 8.4 (q); $v_{max.}$ 1 793m, 1 249m, and 840s cm^{-1}.

2,3,3-Trimethylcyclopropene-1-carboxylic Acid (5; R = Me, X = CO₂H).—Methyl-lithium (10.1 ml; 1.55M) was added over 5 min to a stirred solution of 1,1,3-tribromo-2,2,3-trimethylcyclopropane (2.0 g) in ether at -78 °C. The mixture was allowed to reach 20 °C, and was then cooled again to -50 °C. A rapid stream of carbon dioxide was passed through the solution for 20 min, and the temperature was then allowed to reach 20 °C, while the gas stream was maintained. Work-up as before and removal of the solvent at 14 mmHg gave 2,3,3-trimethylcyclopropene-1-carboxylic acid (0.60 g, 76%) which showed δ_H 11.16 (1 H, br s), 2.25 (3 H, s), and 1.20 (6 H, s). The acid was converted to its methyl ester [δ_H 3.75 (3 H, s), 2.23 (3 H, s), and 1.20 (6 H, s)] by reaction with 1 mol equiv. of diazomethane at -30 °C.[4,11]

2-(2,3,3-Trimethylcycloprop-1-enyl)propan-2-ol (5; R = Me, X = CMe₂OH).—(a) Methyl-lithium (4.5 ml; 1.55M) was added over 5 min to 1,1,3-tribromo-2,2,3-trimethylcyclopropane (1.0 g) in ether (15 ml) at -40 to -50 °C. The mixture was allowed to reach room temperature; after 5 min dry acetone (0.46 ml) was added at -50 °C, when a heavy white precipitate formed. The mixture was again allowed to reach room temperature and after 10 min water (10 ml) was added. The aqueous layer was extracted with ether (2 × 10 ml) and the combined organic layers were washed with water (2 × 10 ml) dried and the solvent was removed at -40 °C and 1 mmHg. The residue was flash distilled at 20 °C and 0.1 mmHg to give 2-(2,3,3-*trimethylcycloprop-1-enyl)propan-2-ol* (0.33 g, 75%) (Found: M^+, 140.1210. $C_9H_{16}O$ requires M, 140.1201) which showed δ_H 1.98 (3 H, s), 1.68 (1 H, s), 1.42 (6 H, s), and 1.13 (6 H, s); $v_{max.}$ 3 380s, 1 860m, and 730m cm^{-1}.

(b) Methyl-lithium (14.0 ml, 1.55M) was added over 5 min to 3-bromo-2,2-dichloro-3,3-dimethylcyclopropane (2.0 g) in ether (20 ml) as in (a), except that the products were stirred at 20 °C for 30 min before the addition of acetone (0.8 ml). Work-up as above gave the alcohol, b.p. 20 °C at 0.1 mmHg (0.75 g, 63%) which was identical by n.m.r. spectrocopy to the sample prepared above.

Reaction of 1,1,3-Tribromo-2,2-dimethylcyclopropane with Methyl-lithium.—(a) Methyl-lithium (50 ml; 1.5M) was added over 10 min to a stirred solution of 1,1,2-tribromo-2,2-dimethylcyclopropane (20.0 g) in ether (150 ml) at -40 °C. The products were quenched by careful addition of water at below -40 °C and the aqueous layer was then washed with ether (3 × 20 ml). The combined ethereal layers were dried and the solvent was removed by distillation at 760 mmHg. Distillation of the residue gave 3-bromo-3-methylbut-1-yne (5.5 g, 58%), b.p. 93—96 °C which was identical by i.r. and ¹H n.m.r. spectroscopy to an authentic sample.[16] A small residue (0.98 g) remained and this also contained a small amount of the alkyne.

(b) The above reaction was repeated at -78 °C and the products were quenched by the addition of water at -50 °C. The organic phase was washed with water (2 × 10 ml) and the solvent was removed at -40 °C and 1 mmHg. The resulting oil was distilled at 0 °C and 14 mmHg to give 1-*bromo-3,3-*

dimethylcyclopropene (5; R = H, X = Br (31%) (Found: M^+, 145.9782. C_5H_7Br requires M, 145.9731) which showed δ_H 7.35 (1 H, s) and 1.22 (6 H, s), contaminated with a trace of ether.

When a solution of the bromocyclopropene was allowed to stand in deuteriochloroform at 20 °C and the products were monitored by n.m.r. spectroscopy, a slow reaction was seen to occur in which the starting material was replaced by 3-bromo-3-methylbut-1-yne over a period of 12 h. When the bromocyclopropene was dissolved in [²H₆]Me₂SO, the starting material had completely disappeared in 10 min at 20 °C and new signals characteristic of 2-methylbut-1-en-3-yne (6: R = H) had appeared.

3,3-Dimethyl-1-trimethylsilylcyclopropene(21; X = SiMe₃).—(a) Methyl-lithium (10.6 ml; 1.55M) was added over 5 min to a stirred solution of 1,1,3-tribromo-2,2-dimethylcyclopropane (2.0 g) in ether (15 ml) under nitrogen at -78 °C. The products were allowed to reach 20 °C and after 30 min were cooled again to -50 °C and treated with trimethylsilyl chloride (1.25 ml) over 5 min. The products were again allowed to reach 20 °C and were then quenched with water (2 ml). Work-up as before followed by removal of the ether at 14 mmHg and 0 °C and distillation at 30 °C and 14 mmHg gave an oil which was one peak on g.l.c. and was characterised as 3,3-*dimethyl-1-trimethylsilylcyclopropene* (0.71 g, 77%) (Found: M^+, 140.1049. $C_8H_{16}Si$ requires M, 140.1021) which showed δ_H 7.9 (1 H, s), 1.2 (6 H, s), and 0.2 (9 H, s); $v_{max.}$ 1 672s cm^{-1}.

(b) Methyl-lithium (12 ml; 1.55M) was added to a stirred solution of 1,1-dibromo-3-chloro-2,2-dimethylcyclopropane (2.0 g) in dry ether (15 ml) at -30 to -40 °C. After 3 min, trimethylsilyl chloride (2 ml) was added at -50 °C. Work-up as before, and analysis of the crude product in ether by n.m.r. spectroscopy, showed a 1:4 mixture of (21; X = SiMe₃) and (21; X = Br). When the reaction was carried out for 5 min at -25 to -20 °C before quenching with trimethylsilyl chloride at -40 °C, the n.m.r. spectrum of the crude product showed only compound (21; X = SiMe₃).

Reaction of 1,1-Dibromo-3-chloro-2,2-dimethylcyclopropane with Methyl-lithium.—(a) Methyl-lithium (9.1 ml; 2.3M) was added over 10 min to a stirred solution of 1,1-dibromo-3-chloro-2,2-dimethylcyclopropane (3.5 g) in ether (30 ml) at -40 to -50 °C. Work-up as before and removal of the solvent at 760 mmHg followed by distillation at 23 °C and 14 mmHg gave a low yield of 3-bromo-3-methylbut-1-yne (18; X = Br) (0.35 g, 18%) identical to that obtained above.

(b) Methyl-lithium (1.6 ml; 1.55M) was added at -90 °C to the trihalide (0.5 g) in ether (10 ml). After 2 min at -75 °C, water (0.5 ml) was added. The products were treated with bromine in carbon tetrachloride at the same temperature until a red colour persisted. Evaporation of the solvent at 14 mmHg gave a single major product identical by g.l.c. and n.m.r. spectroscopy to compound (17; X = Br); an unidentified minor (*ca.* 10%) product was also obtained.

1-Chloro-3,3-dimethylcyclopropene (21; X = Cl).—(a) Methyl-lithium (6.5 ml; 1.55M) was added over 2 min to a stirred solution of 3-bromo-1,1-dichloro-3,3-dimethylcyclopropane (2.0 g) in ether (4 ml) at -50 °C. After 10 min at 20 °C the volatile products were distilled at 14 and 1 mmHg and the distillate was concentrated by distillation at 1 mmHg and -40 °C. The residue consisted of a solution of 1-chloro-3,3-dimethylcyclopropene in ether. The cyclopropene showed signals at δ_H 7.4 (1 H, s) and 1.2 (6 H, s), and at δ_C 129.5 (s), 114.4 (d), 29.8 (s), and 26.6 (q). The ¹³C n.m.r. spectrum showed *only* the above signals apart from those of ether.

(b) The above reaction was repeated at -50 °C. After 2 min, water was added at -50 °C; g.l.c. showed that no reaction had

occurred. However, when the reaction was carried out for 5 min at 0 °C the worked up by the addition of water at − 10 °C, g.l.c. showed complete reaction of the starting material.

Reaction of 3-Bromo-1,1-dichloro-2,2-dimethylcyclopropane with an Excess of Methyl-lithium.—(a) Methyl-lithium (14.9 ml; 1.55M) was added slowly under nitrogen to 3-bromo-1,1-dichloro-2,2-dimethylcyclopropane (4; X = Br) (2.0 g) and 2,3-dimethylbut-2-ene (1.6 g) in ether (15 ml) at − 78 °C. The products were allowed to reach 20 °C and after 1 h were quenched with water (2 ml). Work-up as above and removal of the solvent at 14 mmHg and 0 °C gave a yellow oil which was one spot on t.l.c. and was purified by distillation at 0.3 mmHg and 50 °C and shown to be identical by n.m.r. spectroscopy and t.l.c. to authentic tetramethyl(2-methylprop-1-enylidene)-cyclopropane (29)[17] (0.95 g, 70%).

(b) The above reaction was repeated except that after 1 h at 20 °C the products were cooled to − 50 °C and treated with trimethylsilyl chloride (1.76 ml) before being allowed to reach 20 °C again and quenching with water. The organic layer was extracted as before. The remaining yellow oil (0.42 g) was one major spot by t.l.c. and by n.m.r. spectroscopy the major component was tetramethyl(2-methylprop-1-enylidene)cyclopropane (29). A number of minor signals were also observed, but none were seen in the olefinic region as would have been expected for (21; X = SiMe₃).

[12]C-*Labelled 3-Bromo-1,1-dichloro-2,2-dimethylcyclopropane* (23).—Sodium hydroxide (3 ml; 50%) was stirred for 18 h at 20 °C with 1-bromo-2-methylprop-1-ene (4.0 g), [^{12}C]chloroform (1.0 g) and cetrimide (200 mg) in dichloromethane (8 ml). The products were washed with 10% hydrochloric acid and the aqueous layer was extracted with dichloromethane (3 × 15 ml). After having been washed with water, the combined organic layers were dried and the solvent was removed at 14 mmHg and 20 °C to give [1-^{12}C]-3-bromo-1,1-dichloro-2,2-dimethylcyclopropane (1.2 g, 64%) which was identical by [1]H n.m.r. spectroscopy to the unlabelled compound; the ^{13}C spectrum was also essentially identical to that of compound (22; X = Br)[13] apart from the absence of the peak at δ_C 68 (C-1).

Preparation and Decomposition of ^{12}C-Labelled 1-Chloro-3,3-dimethylcyclopropene (24).—(a) The trihalide (23) was treated with 1.2 mol equiv. of methyl-lithium in ether at − 50 °C as described above for the unlabelled compound. After having been quenched with water, and worked up as for (21; X = Cl) above, the remaining solution of 1-chloro-3,3-dimethylcyclopropene (24) in ether was examined by [13]C n.m.r. spectroscopy. The spectrum was identical to that for the unlabelled compound (21; X = Cl) except that the signal at δ_C 129.5 was not present.

(b) Solutions of compounds (24) and (21; X = Cl) in ether were diluted with deuteriochloroform and allowed to stand at 20 °C in the dark. The products were then examined by [13]C n.m.r. spectroscopy. After 14 days the unlabelled compound had rearranged to give compound (18; X = Cl) which showed all the signals present in the spectrum of an authentic sample [86.7 (s), 66.0 (d), 56.8 (s), and 34.6 (q)].[21] The rearrangement of the labelled compound proceeded rather more rapidly, and was complete in ca. 7 days, perhaps because the concentration of cyclopropene relative to ether was higher. In this case the product showed all the signals expected for compound (18; X = Cl), except for that at δ_C 86.7.

1-*Bromo-2,3-dimethylcyclopropene* (16; X = Br).—Methyl-lithium (8.9 ml; 2.3M) was added over 2 min to a stirred solution of cis-2,3-dimethyl-1,1,2-tribromocyclopropane (4.0 g) in ether (35 ml) at − 40 to − 50 °C. After quenching with water at that temperature the products were allowed to reach ambient

temperature and were worked up as above to give 1-bromo-2,3-dimethylcyclopropene, b.p. 19 °C at 14 mmHg (250 mg, 31%) (Found: M⁺, 145.9739. C₅H₇Br requires M, 145.9731) which showed δ_H 1.8—2.3 (1 H, m), 2.05 (3 H, s), and 1.10 (3 H, d, J 5 Hz); $\nu_{max.}$ 1 830m and 76s cm⁻¹. A residue remained from the distillation (430 mg) which appeared to be a complex mixture by n.m.r. spectroscopy.

1,3-*Dimethyl-2-trimethylsilylcyclopropene* (16; X = SiMe₃).—(a) Methyl-lithium (10.6 ml; 1.55M) was added slowly to a stirred solution of 1,1,2-tribromo-2,3-dimethylcyclopropane (2.0 g) in ether (15 ml) at − 78 °C under nitrogen. The mixture was allowed to reach 20 °C and after 10 min was cooled to − 50 °C and trimethylsilyl chloride (1.25 ml) was added over 5 min. The products were again allowed to reach 20 °C and after 20 min water (2 ml) was added carefully. The aqueous layer was extracted with ether (3 × 20 ml) and the combined organic layers were dried and evaporated at 14 mmHg. The remaining oil was distilled at 4 mmHg and 20 °C and characterised as 1,3-dimethyl-2-trimethylsilylcyclopropene (0.65 g, 71%) (Found: M⁺, 140.1020. C₈H₁₆Si requires M, 140.1021) which was one peak on g.l.c. and showed δ_H 2.08 (3 H, s), 1.23 (1 H, q, J 4.5 Hz), 0.92 (1 H, s), 7.40 (1 H, br s), and 1.28 (6 H, s); $\nu_{max.}$ 3 600—2 300v br, 1 741s, and 1 687s cm⁻¹.

3,3-*Dimethylcyclopropene-1-carboxylic   Acid*—Methyl-lithium (16.4 ml; 1.6M) was added at − 78 °C to a solution of 1,1,2-tribromo-3,3-dimethylcyclopropane (3.66 g) in dry ether (10.0 ml). The mixture was allowed to warm to 0 °C; after 10 min it was cooled to − 50 °C and rapid stream of CO₂ was passed through the solution for 20 min. The mixture was allowed to warm to 20 °C, a slow stream of CO₂ being maintained. Water (20 ml) was added carefully at − 40 °C and after all the precipate was dissolved, the aqueous layer was separated and acidified with HCl (15.0 ml; 10%). Ether (30 ml) was added and the organic layer was dried (MgSO₄) and the solvent was removed at 14 mmHg at 20 °C to give 3,3-dimethylcyclopropene (0.95 g, 71.14%) (Found: M⁺, 112.0513. C₆H₈O₂ requires M, 112.0514) as a yellow oil showed δ_H 1.28 (6 H, s), 7.4 (1 H, br s), and 8.03 (1H, s,); $\nu_{max.}$ 1 741 and 1 687 cm⁻¹.

This acid was unstable at 20 °C and on one occasion after 10 min underwent an exothermic reaction to give an unidentified product, while at − 20 °C it is stable for more than 10 days in ether solution.

Reaction of the acid with one equivalent of diazomethane at − 30 °C led to a mixture of starting material, its methyl ester which gave a [1]H n.m.r. spectrum identical to that reported,[18] and the corresponding pyrazoline.[19] These could be separated by column chromatography but the ester was more efficiently prepared as below.

Methyl   3,3-Dimethylcyclopropene-1-carboxylate.—Methyl-lithium (15.7 ml, 1.6M) was added over 10 min to a stirred solution of 1,1-dibromo-3-chloro-2,2-dimethylcyclopropane (3.0 g) in ether (15 ml) at − 78 °C. The products were allowed to reach 0 °C and after 10 min were added over 5 min to methyl chloroformate (4.4 ml) in ether (15 ml), maintaining the temperature below 30 °C. After 5 min the products had been quenched with water (30 ml) and the aqueous layer extracted with ether (20 ml), the combined organic layers were washed with water (2 × 20 ml), dried and the solvent was evaporated at 14 mmHg and then 1 mmHg (25 °C). The residue was distilled to give methyl 3,3-dimethylcyclopropene-1-carboxylate, b.p. 30 °C at 0.1 mmHg (1.1 g, 69%) identical to that above. The product was stored in chloroform solution at − 20 °C.

Acknowledgements

References

1 For a review see P. Weyerstahl, 'Dihalocyclopropanes,' in The Chemistry of Functional Groups, eds. S. Patai and Z. Rappoport, Suppl. D.

2 L. Skattebøl, Acta Chem. Scand., 1963, 17, 1683.

3 For related papers see M. S. Baird and P. D. Slowey, Tetrahedron Lett., 1982, 3795; M. S. Baird and H. Hussain, J. Chem. Res., 1985, (S) 182, (M) 2061.

4 G. L. Closs, 'Cyclopropenes,' in Advances in Alicyclic Chemistry, vol. 1, 1966.

5 See e.g., W. E. Billups, T. C. Shields, W. Y. Chow, and N. C. Deno, J. Org. Chem., 1972, 23, 3676.

6 L. S. Crombie, P. J. Griffiths, and B. J. Walker, J. Chem. Soc., Chem. Commun., 1969, 1206.

7 T. C. Shields, B. A. Loving, and P. D. Gardner, J. Chem. Soc., Chem. Commun., 1967, 556.

8 T. C. Shields and W. E. Billups, Chem. Ind. (London), 1967, 1999.

9 G. Frenking, L. Hülskämper, and P. Weyerstahl, Chem. Ber., 1982, 115, 2826; K.-O. Henseling and P. Weyerstahl, ibid., 1975, 108, 2803; A. Jonzyk and T. Radwan-Pytlewski, J. Org. Chem., 1983, 48, 912; T. Greibrokk, Acta Chem. Scand., 1973, 27, 3207.

10 See e.g. T. Chan and D. Massuda, Tetrahedron Lett., 1975, 3383; W. E. Billups, E. W. Casserly, and B. E. Arney, J. Am. Chem. Soc., 1984, 106, 440; Tetrahedron Lett., 1984, 3935.

11 G. L. Closs and L. E. Closs, J. Am. Chem. Soc., 1961, 83, 1003 and 2015; 1963, 85, 99.

12 M. S. Baird, S. R. Buxton, and J. S. Whitley, Tetrahedron Lett., 1984, 1509.

13 M. S. Baird, W. Nethercott, and P. D. Slowey, J. Chem. Res., 1985, (S) 370.

14 A. J. Schipperijn and P. Smael, Rec. Trav. Chim., 1973, 92, 1159.

15 S. Raucher, Tetrahedron Lett., 1977, 3909.

16 V. J. Shiner and J. S. Humphrey, J. Am. Chem. Soc., 1967, 89, 622.

17 See e.g., M. S. Baird, Tetrahedron Lett., 1984, 4829.

18 See e.g., N. Galloway, B. R. Dent, and B. Halton, Aust. J. Chem., 1982, 36, 593; C. Dietrich-Buchecker and M. Franck-Neumann, Tetrahedron, 1977, 33, 751.

19 M. S. Baird and H. H. Hussain, unpublished results.

20 G. J. Martin and M. L. Martin, J. Chim. Phys., 1964, 61, 1222.

21 G. F. Hennion and A. P. Boisselle, J. Org. Chem., 1961, 26, 725.