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The Generation and Trapping of 1,2-Dibromo-3-methylbut-2-en-1-ylidenes

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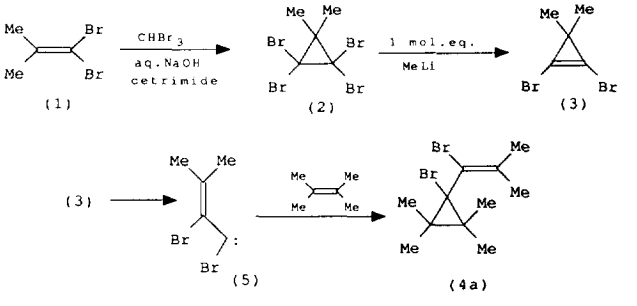
Abstract: *1,2-Dibromo-3,3-dimethylcyclopropene, generated by debromination of 1,1,2,2-tetrabromo-3,3-dimethylcyclopropane on reaction with methyllithium, ring-opens at 0 - 20 °C to produce 1,2-dibromo-3-methylbut-2-en-1-ylidene. This is trapped by alkenes to give vinylcyclopropanes. In the case of electron rich alkenes, the stereochemistry is retained in the product, suggesting that a singlet carbene is involved. In the case of α,β-unsaturated esters, ketones or nitriles, the major cyclopropane produced has the vinyl and electron-withdrawing groups cis-related. 3-(2-Methoxy-ethyl)-3-methyl- and 3-(2-bromoethyl)-3-methyl-1,2-dibromocyclopropenes also ring-open at ambient temperature but little stereoselectivity is observed in the trapping of the derived vinyl-carbenes by alkenes. The reaction of 3-(2-hydroxyethyl)-3-methyl-1,1,2,2-tetrabromocyclopropane with methyl lithium or diethylphosphite and triethylamine does not lead to an isolable cyclo-propene, but instead to Z-1,2-dibromo-3-methylbuta-1,3-diene; quenching with deuterium oxide at low temperature leads to the incorporation of deuterium at C-1.*

We have shown that 3,3-disubstituted 1,2-dichlorocyclopropenes rearrange at ambient temperature to vinylcarbenes which are trapped by electron-rich alkenes with retention of stereochemistry, by α,β-unsaturated esters, by alkynes, phosphaalkynes and ethers.[1-5] Moreover, 3-monoalkyl-1,2-dibromocyclopropenes[6] and 1,2-dibromocyclopropene itself[7] ring-open to the corresponding carbenes under similar conditions. The stereochemistry of the ring-opening when the 3-substituents are different has been the subject of semi-empirical calculations.[8] A brief account of the ring-opening of 1-bromo-2-chloro-3,3-dimethylcyclopropene has appeared, but this reaction is of limited synthetic value because both 1-chloro-2-bromo-3-methylprop-2-en-1-ylidene and the 1-bromo-2-chloro- isomer are trapped to an almost equal extent.[9] We now describe the generation and ring-opening of 1,2-dibromo-3,3-dimethylcyclopropene and related compounds.

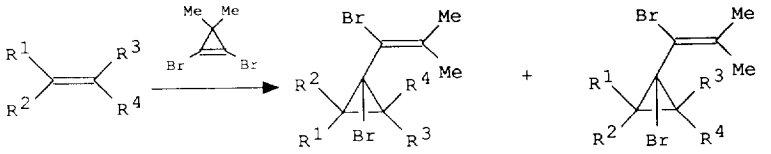
Reaction of 1,1-dibromo-2-methylpropene (1) with bromoform, 50% aqueous sodium hydroxide and cetrimide led to 3,3-dimethyltetrabromocyclopropane (2) (50%). Treatment of this with 1.1 mol.equiv. of methyl lithium in ether led to the cyclopropene (**3**) which showed a singlet in its ^{1}H n.m.r.spectrum at δ 1.27. It could be stored for several days at liquid nitrogen temperature but after 5 min at 20 °C a solution in chloroform had undergone considerable decomposition. If the reaction was repeated in the presence of 2,3-dimethylbut-2-ene and the resulting solution was allowed to stand for 3 h at 20 °C, dibromide (**4a**) was obtained (87%).



Compound (**4a**) showed six signals in the ^{1}H n.m.r. spectrum, in agreement with a preferred conformation in which the vinyl-group is not bisecting the cyclopropane ring; similar twisted conformations have been

reported for related vinylcyclopropanes including the analogue of (**4a**) in which the bromines are replaced by chlorines.[1,2,10] Compound (**4a**) apparently arises by ring-opening of (**3**) to the vinylcarbene (**5**), and addition of this to the alkene. Reaction of the dihalogenocyclopropene (**3**) with a series of other alkenes also led to the trapping of the carbene (**5**) to give cyclopropanes (**4**) (and (**6**)) (Table).

TABLE. Reaction of 1,2-dibromo-3,3-dimethylcyclopropene with alkenes



(4) (6)

R^1	R^2	R^3	R^4	Method	Product	%
Me	Me	Me	Me	a	4a	87
Me	Me	H	H	a	4b	92
Me	H	H	Me	a	4c	58
Me	H	Me	H	a	4d,6d	86[+]
Me	CO_2Me	H	H	b	4e	88
H	CO_2Me	H	H	b	4f	70
H	CN	H	H	b	4g,6g	37[++]
H	MeCO	H	H	b	4h	34

a: The cyclopropene was generated by reaction of (**2**) with methyllithium at -70 °C in the presence of the alkene, and the products were allowed to reach 20 °C; b: The cyclopropene was generated in ether solution by reaction of (**2**) with methyllithium at -70 °C followed by products quenching with water; the alkene was then added; [+] Ratio 5:1;[++] Ratio 3:1.

The ^1H n.m.r. spectrum of cyclopropane (**4b**) showed the presence of two rotamers about the cyclopropane to alkene bond in ratio ca. 7:4.[11] The ^{13}C spectrum also showed two sets of signals. In the same way (**4c**) showed two rotamers in an ca. 3:4 ratio when the ^1H n.m.r. was run at 20 °C. At 100 °C, however, the spectrum showed just four broad signals corresponding to intermediate rate rotation on the n.m.r. timescale, and the rotation barrier was estimated as 19 kcal mol^{-1} using the approximation of Gunther.[12]

Addition of the cyclopropene to *cis*-but-2-ene led to a mixture of isomers (**4d**) and (**6d**). The proton n.m.r. spectrum of the mixture at room temperature was very difficult to interpret. However the spectra at low and at high temperature were consistent with the presence of a minor isomer, the spectrum of which did not change with temperature and a major isomer which showed restricted rotation at low temperature, intermediate rate rotation at room temperature and rapid rotation on the n.m.r. timescale at high temperature. Thus the spectrum of the major isomer (**4d**) at -55 °C showed one singlet for the two olefinic methyls at δ 1.85. At high temperature this singlet became two separate three hydrogen singlets. The signals for the ring methyls at low temperature were a doublet at δ 1.15 which was coupled to a broad pentuplet at δ 1.35 and a broad singlet at δ 1.08 which was presumed to be covering the signals for the second ring hydrogen. At 100 °C, the two methyl signals became a single broad doublet at δ 1.25-1.27 and the two ring protons became a single broad multiplet at δ 1.41. At room temperature, the spectrum was broad in places and intermediate between these extremes. The rotation barrier was calculated as ca. 12 Kcal mol^{-1}.[12] The spectrum for the minor isomer (**6d**) did not change with temperature and showed restricted rotation, consistent with this being the isomer with the two methyl groups *cis* to the large alkenyl substituent. The signals for the ring methyls appeared upfield to those in the major isomer, in agreement with their position in the shielding zone of the vinyl group.

There was no evidence for the presence of any *trans* isomer (**4c**) in the reaction of the vinylcarbene (**5**) with *cis*-but-2-ene, nor of any (**4d**) or (**6d**) in its reaction with *trans*-but-2-ene. This is consistent with a concerted addition of a singlet carbene.[13]

Trapping the vinylcarbene (**5**) with methyl acrylate afforded compound (**4f**), the proton and ^{13}C n.m.r.

spectra of which at room temperature were consistent with an ca 1.7:1 mixture of two rotamers. On heating to 60 °C, the proton n.m.r. spectrum became simpler due to rapid rotation on the n.m.r. timescale, showing one singlet at δ 3.6 for the methoxy group and one singlet at δ 1.8 for one olefinic methyl, as well as a very broad signal at δ 1.9-2.2 for the three cyclopropyl protons and the second olefinic methyl group. The stereochemistry of this compound was assigned as having the ester and vinyl groups *cis*- related by analogy with the corresponding dichloro-compound.[1] There was a small additional singlet in the methoxy region (<5% of the signal for the major rotamer) although no signals could be seen at higher field; this may correspond to the presence of a small amount of the isomer with vinyl and ester groups *trans* to each other.

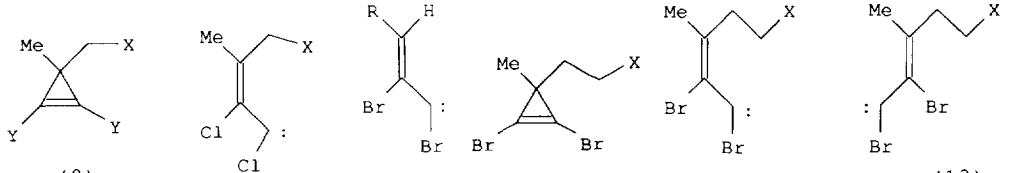
When the vinylcarbene was trapped with methyl methacrylate, the cyclopropane (**4e**) was obtained in 88% yield. Again the proton and ^{13}C n.m.r. spectra at room temperature were consistent with an ca. 1:1 mixture of two rotamers, but because of the ratio, it was not possible to assign all the peaks to one particular rotamer. On heating to 100 °C in deuterated nitrobenzene the ^{1}H n.m.r. spectrum became broad and the signals began to coalesce. At this temperature, there was a single broad methoxy signal at δ 3.7, two broad methyl signals at δ 1.85 and 1.75 and broad singlets at δ 2.6, 2.55, 2.0 and 1.45. The integrals were not completely clear suggesting additional signals were hidden underneath the spectrum. Nonetheless the doubling up of the signals in the room temperature spectrum had been removed and was therefore due to the presence of two rotamers rather than diastereoisomers. There was a small additional singlet in the methoxy region (<5% of the signal for the major isomer) but no signals could be discerned at higher field to correspond to a minor diastereoisomer.

Addition of the vinylcarbene (**5**) to acrylonitrile led to compounds (**4g**) (28 %) and (**6g**) (9 %). The proton n.m.r. spectrum of (**4g**) at room temperature showed very broad signals at δ 2.58 and 2.09 plus one singlet at 1.96. When the spectrum was run at -55°C, it showed the presence of two rotamers in the ratio of ca 3:2. The cyanide group of (**4g**) was converted into the corresponding ester by treating it with gaseous HCl in methanol. This was identical to those of the ester (**4f**) prepared by trapping the vinylcarbene (**5**) with methyl acrylate, confirming that the major isomer of (**4g**) had cyanide and alkene groups cis-related.

Addition of the vinylcarbene (**5**) to methyl vinyl ketone led to compound (**4h**). The ^{13}C n.m.r. spectrum showed the expected nine major signals including a carbonyl carbon at δ 200 and two alkene signals at δ 140 and 118, but the proton n.m.r. spectrum indicated the presence of a second rotamer of the product in the ratio of ca. 1:4. In order to establish the stereochemistry of this compound it was converted to the corresponding 2,4-dinitrophenyl)hydrazone (**7**) by treatment with 2,4-dinitrophenylhydrazine. An X-ray crystallographic determination of the structure of (**7**) showed that the ketone and vinyl groups in (**4h**) were *cis*-related as given below.[#] Because the crystals were very small, the structure was not completely refined and indicated a chlorine rather than a methyl group on one alkene position; details of this determination will be presented elsewhere. The proton n.m.r. spectrum of the hydrazone was once again highly dependent on temperature and consistent with the presence of two rotamers which undergo relatively rapid interconversion at 60 °C.

The results reported above show that 1,2-dibromo-3,3-dimethylcyclopropene ring-opens in a manner very similar to that for the corresponding 1,2-dichloride and that the derived carbene is trapped by electron-rich alkenes with retention of alkene stereochemistry, in agreement with the trapping of a singlet carbene. The preferential formation of products (**4**) with ester groups cis- to the alkene which has been reported in additions of other 1,2-dihalogenoprop-2-en-1-ylidenes is also clearly seen in the corresponding additions to an α,β-unsaturated ketone and a nitrile. The origin of this effect is still not clear.[4]

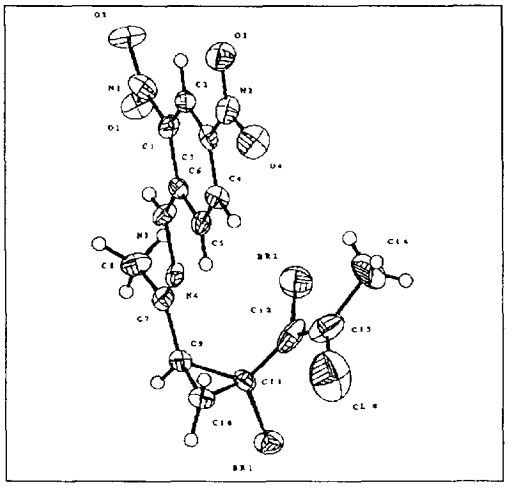
The ring-opening of the dichlorides (**8**, Y = Cl, X = Cl, OMe, Ph) has been shown to lead to the trapping of single stereoisomers of the vinylcarbenes (**9**) by added alkenes.[2,3]

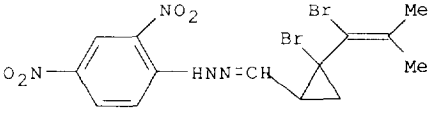


The origin of this stereocontrol has been explained in terms of an interaction between the developing carbene centre and an antibonding orbital of the C-X bond.[8] In the case of 3-monoalkyl-1,2-dibromocyclopropenes, the carbene (**10**) which is trapped has the alkyl substituent trans- to the carbene centre,

and the selectivity can be explained in steric terms.[8] It was of interest therefore to determine whether the ring-opening of cyclopropenes (**11**) would be controlled by the presence of the more distant X-group and lead to a preferred stereoisomer of the carbenes (**12**) or (**13**).

X-Ray Crystallographic Structure of (7)

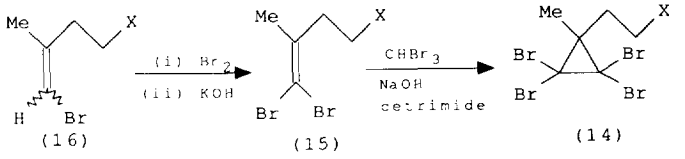




(7)

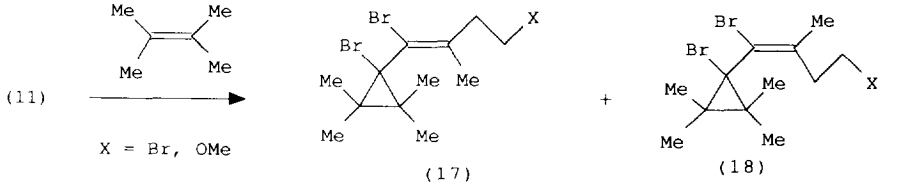
* Incomplete refinement. Should be CH_3

The cyclopropanes (**14**, X = OH, Br, OMe) were prepared by dibromocyclopropanation of the corresponding alkenes (**15**, X = $OCMe_2OMe$, Br, OMe)[14] under phase transfer conditions. Compound (14, X = OMe) could also be prepared by alkylation of (**14**, X = OH). Reaction of the cyclopropanes (**14**, X = Br, OMe) with 1.1 mol.equiv. of methyl lithium in ether led to the corresponding cyclopropene (**11**, X = Br, OMe) as unstable liquids;[##] if these were allowed to stand in chloroform at room temperature they decomposed over a period of 3 - 5 h at ambient temperature and no products were identified.



(16) (15) (14)

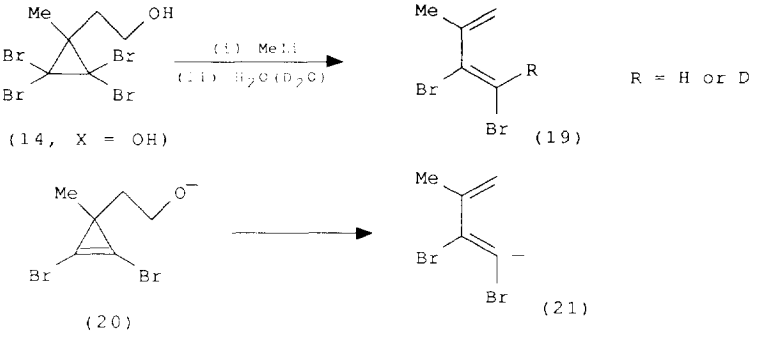
If the reactions were carried out in the presence of 2,3-dimethylbut-2-ene and the products were allowed to stand for several hours at room temperature, the cyclopropanes (**17**, X = Br, OMe) and (**18**, X = Br, OMe) were obtained in ca. 2:1 and 4:3 ratio respectively.



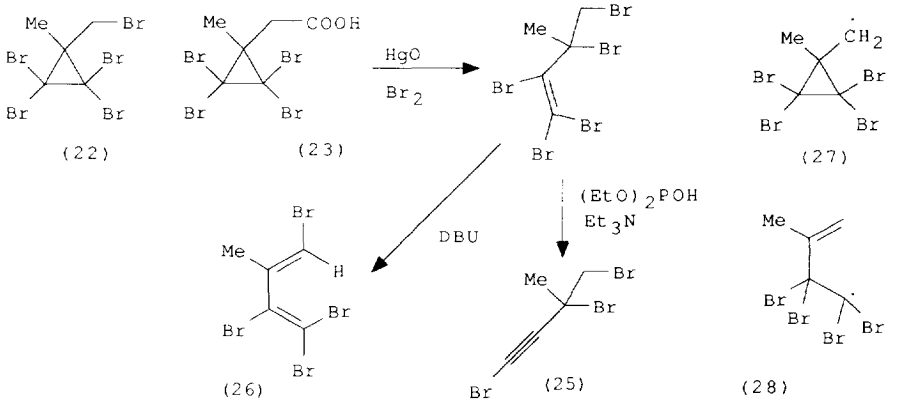
(11) X = Br, OMe (17) (18)

When the alcohol (**14**, X = OH) was treated with 2.2 mol.equiv. methyllithium as above, no cyclopropene was isolated; instead the product after quenching with water was the dibromodiene (**19**, R = H).[15] This may be rationalised in terms of the formation of (**20**) and fragmentation to the anion (**21**); indeed, if the

reaction was worked up by addition of D_2O, the product was the deuterated diene (**19**, R = D) with an incorporation of ca. 75 %. The anion could not, however, be trapped by addition of carbon dioxide or trimethylsilyl chloride, the diene (**19**, R = H) being isolated in each case. The diene (**19**, R = H) was also obtained (40 %) when (**14**, X = OH) was debrominated with diethylphosphite and triethylamine.[17] A related fragmentation has been reported in the case of the reaction of (1,1,2,2-tetrachloro-3-methylcycloprop-3-yl)methanol with methyl lithium.[16]



In order to compare the reactivity of (**8**, Y = Cl) with the corresponding dibromides (**8**, Y = Br), the preparation of the cyclopropane precursor (**22**) was examined. It was anticipated that a Hunsdieker reaction on the acid (**23**) would lead to (**22**); however, treatment of (**23**), derived by oxidation of the alcohol (**14**, X = OH), with red mercuric oxide and bromine in carbon tetrachloride lead instead to the pentabromide (**24**).* This may be derived by generation of the corresponding cyclopropylmethyl radical (**27**) by decarboxylation, and fragmentation of this to (**28**).[19] Loss of a bromine atom, followed by the addition of bromine to the disubstituted alkene would then lead to (**24**).**



Experimental Section

Commercial reagents were used without further purification unless otherwise stated. Dichloromethane was distilled over calcium hydride. Diethyl ether and tetrahydrofuran were distilled over sodium wire. Petroleum ether was of boiling point 40 - 60 °C and was purified by distillation. Capillary Glc was conducted using a Perkin-Elmer F17 F.I.D. Tlc was performed using Aldrich silica gel 60 (F254) plates. Compounds were visualised either under an ultraviolet source or by exposure to iodine vapour. Column chromatography was conducted with Merck 7736 silica gel under medium pressure. Melting points are uncorrected. Infrared spectra were obtained as KBr discs (solids) or as liquid films on a Perkin-Elmer 1600 FTIR spectrometer. Low resolution mass spectra were obtained using a Finnigan Mat 1020 spectrometer. Mass measurements reported refer to the ^{79}Br isotope unless otherwise stated; measured masses were obtained from the Swansea Mass

Spectrometry Service. Microanalyses were performed with a Carlo-Erba Model 1106 CHN analyser. Nmr spectra were recorded using a Brucker AC250 at 250 MHz for protons and 62.5 MHz for carbon and in the latter case were either broad-band or gated decoupled. Reactions requiring anhydrous conditions were performed using oven dried glassware (250 °C) that was cooled under a stream of either dry nitrogen or argon and the experiments were conducted under a positive atmosphere of one of these gases. Yields quoted are for the purified compounds unless otherwise stated.

3,3-dimethyl-1,1,2,2-tetrabromocyclopropane

Sodium hydroxide (10 mol.equiv., 20 g) in water (20 ml) was added carefully to a rapidly stirred solution of 1,1-dibromo-2-methylprop-1-ene (12.26 g, 0.057 mol) in dichloromethane (30 ml), bromoform (1.5 mol.equiv., 7.5 ml) and cetrimide (1 g) at room temperature. After 12 hours, dichloromethane (300 ml) was added followed by brine (300 ml) and the product was extracted with dichloromethane. The combined organic layers were dried ($MgSO_4$) and the solvent was removed at 14 mm Hg. The residue was stirred with ether (250 ml) for 15 mins, and precipitated cetrimide was filtered off. The solvent was removed at 14 mm Hg to give the crude product (11 g, 50 %) which was recrystallised from hot methanol to give **3,3-dimethyl-1,1,2,2-tetrabromocyclopropane,** m.p. 120-121 °C ($C_5H_6Br_4$ requires: C 15.54; H 1.57. Found C 15.73; H 1.54 %) which showed δ_H 1.5 (6H, s); δ_C 49.4, 37.2, 25.8; υ_{max} 2900 w, 1451 s, 762 s; m/e 303, 305, 307, 309 (M-Br).

Preparation of 1,2-Dibromo-3,3-dimethylcyclopropene

A solution of 3,3-dimethyl-1,1,2,2-tetrabromocyclopropane (0.5 g, 0.0013 mole) in dry ether (10 ml) was treated with methyllithium (1.05 mol.equiv., 1.5M, 0.9 ml) at -70 °C under an atmosphere of inert gas. The mixture was allowed to reach -20 °C, cooled -50 °C and treated with water (2 ml); the ether layer was decanted from the ice, which was washed with ether (3 x 15 ml). Evaporation of ether at -30 to -40 °C and 0.6 mm Hg afforded a colourless liquid identified as 1,2-dibromo-3,3-dimethylcyclopropene (**2**) (δ_H 1.27 (6H, s)) which was stable for several days at liquid nitrogen temperature but after 5 mins at room temperature, the ^1H n.m.r. spectrum gave complex signals showing that the cyclopropene had decomposed.

Preparation of Dibromopropenylcyclopropanes

Method A

(a) **2-Bromo-2-(1-bromo-2-methylprop-1-enyl)-1,1,2,2-tetramethylcyclopropane:** Methyllithium (1.0 mol.equiv., 1.5M, 0.86 ml) was added to a stirred solution of 3,3-dimethyl-1,1,2,2-tetrabromocyclopropane (0.5 g, 0.0013 mole) in dry ether (10 ml) and 2,3-dimethylbut-2-ene (10 mol.equiv., 1.54 ml) at -70 °C. The reaction mixture was allowed to reach room temperature, stirred for 3 hours and then quenched with water (2 ml) at -50°C and the product was extracted with ether (3 x 15 ml), dried ($MgSO_4$) and the solvent removed at 14 mm Hg to give solid **2-bromo-2-(1-bromo-2-methylprop-1-enyl)-1,1,2,2-tetramethylcyclopropane (4a)** (0.35 g, 87 %). It was purified by column chromatography eluting with petrol and ether (5:0.5), m.p. 50-52 °C ($C_{11}H_{18}Br_2$ requires: C 42.58; H 5.9. Found: C 42.32; H 6.0 %) which showed δ_H 1.86 (3H, s), 1.80 (3H, s), 1.33 (3H, s), 1.24 (3H, s), 1.19 (3H, s), 1.13 (3H, s); δ_C 139.0, 123.9, 49.3, 31.4, 27.8, 25.6, 25.1, 22.6, 22.3, 20.3, 19.2; υ_{max} 3002 s, 2919 s, 1631 s, 1449 s, 753 s; m/z 293/295/297 (M-CH_3).

(b) **2-Bromo-2-(1-bromo-2-methylprop-1-enyl)-1,1-dimethylcyclopropane:** The procedure in (a) was repeated using isobutylene (10 mol.equiv., 0.73 g) instead of 2,3-dimethylbut-2-ene to give **2-bromo-2-(1-bromo-2-methylprop-1-enyl)-1,1-dimethylcyclopropane (4b)** (0.33 g, 92 %) ($C_9H_{14}Br^{79}Br^{81}$ requires: 281.9438. Found: 281.9442) the n.m.r. of which showed (r.t.) signals for two rotamers in ratio 7:4. The major rotamer showed δ_H 1.89 (3H, s), 1.86 (3H, s), 1.46 (3H, s), 1.22 (1H, d, J 6.5 Hz), 1.17 (1H, d, J 6.5 Hz), 1.12 (3H, s). The minor rotamer showed δ_H 1.94 (3H, s), 1.86 (3H, s), 1.40 (3H, d, J 6.1 Hz), 1.39 (3H, s), 1.29 (1H, d, J 6.1 Hz), 1.22 (3H, s); δ_C 139.6, 136, 123.7, 122.6, 48.9, 49.0, 33.9, 33.3, 30.9, 25.7, 25.5, 25.2, 22.5, 22.4, 22.3, 21.8, 20.1; υ_{max} 2917 s, 1636 s, 1435 s, 670 s; m/z 280, 282, 284 (M), 265, 267, 269 (M-CH_3).

(c) **2-Bromo-2-(1-bromo-2-methylprop-1-enyl)-trans-1,2-dimethylcyclopropane:** The above procedure was repeated using *trans*-butene (10 mol.equiv., 0.73 g) in place of 2-methylpropene as the trapping alkene. **2-Bromo-2-(1-bromo-2-methylprop-1-enyl)-*trans*-1,2-dimethylcyclopropane (4c)** was obtained (0.21 g, 58.3 mmole) ($C_9H_{14}Br^{79}Br^{81}$ requires: 281.9438. Found: 281.9442) which gave a single peak by g.l.c. but the ^1H n.m.r. spectrum showed signals for two rotamers in ca. 3:4 ratio. The spectrum showed δ_H 1.89 (3H, s) and 0.79-0.71 (1H, dq) (for both rotamers); 1.84 (3H, s), 1.43 (3H, d, J 6.2 Hz), 1.17 (4H, br) (major rotamer);

1.96 (3H, s), 1.64 - 1.56 (1H, br.m), 1.31 (3H, d, J 6.2 Hz), 1.12 (3H, d, J 6.4 Hz) (minor rotamer); δ_H (at 100°C, in perdeuteronitrobenzene) 2.0 (3H, br.s), 1.9 (3H, s), 1.3 - 1.5 (ca 4H, br.s), 1.0 - 1.2 (3H, br.s), 0.7 - 0.9 (1H, v.br); δ_C 140.0, 138.0, 123.3, 120.0, 50.0, 48.0, 37.5, 32.5, 31.3, 30.7, 29.7, 25.4, 25.3, 22.6, 21.9, 17.1, 16.8, 15.2; υ_{max} 2925 s, 1635 s, 1449 s, 701 s; m/z 280, 282, 284 (M), 265, 267, 269 (M-CH_3).

(d) 3-Bromo-3-(1-bromo-2-methylprop-1-enyl)-*cis*-1,2-dimethylcyclopropanes: The above procedure was repeated using *cis*-butene (1.0 mol.equiv., 0.73 g) as the trapping alkene. 2-Bromo-2-(1-bromo-2-methylprop-1-enyl)-*cis*-1,2-dimethylcyclopropane was obtained (0.31 g, 86 %) ($C_9H_{14}Br^{79}Br^{81}$ requires: 281.9438. Found: 281.9442) which gave two components (**4d and 6d**) in ca.5:1 ratio by g.l.c., but no product identical to that from (c) above. The major isomer showed signals at 1.85 (6H, s), 1.26 (2H, br), 1.14 - 1.12 (6H, br.d). The minor isomer showed signals at 1.93 (3H, s), 1.87 (3H, s), 1.07 (3H, d, J 6.6 Hz), 1.06 (3H, d, J 6.6 Hz); (δ_H at 100 °C, in perdeuteronitrobenzene) the major isomer showed signals at 2.0 (3H, s), 1.92 (3H, s), 1.41 (2H, br.m), 1.27 - 1.25 (6H, br.d). The minor isomer showed δ_H 2.05 (3H, s), 1.96 (3H, s), 1.21 (3H, d, J 6.7 Hz), 1.15 (3H, d, J 6.6 Hz) (the ring hydrogens could not be identified); δ_H (at -55 °C) (major isomer) 1.85 (6H, s), 1.35 (1H, br.pent), 1.15 (3H, d, J ca 6 Hz), 1.08 (4H, br.s); δ_C 137.4, 126.4, 119, 53.3, 31.0, 30.9, 27.8, 25.7, 25.3, 22.9, 21.7, 11.5, 10.4, 9.8, plus a few minor signals; υ_{max} 2999.9 s, 2955 s, 1637.7 s, 1449 s, 687 s; m/e 280, 282, 284 (M), 265, 267, 269 (M-CH_3).

Method B

(a) Methyl 2-bromo-2-(1-Bromo-2-methylprop-1-enyl)cyclopropanecarboxylate: Methyllithium (1.0 mol.equiv., 1.5 M, 0.86 ml) was added to a stirred solution of 3,3-dimethyl-1,1,2,2-tetrabromocyclopropane (0.5 g, 0.0013 mole) in dry ether (10 ml) at -70 °C. The reaction mixture was stirred while temperature was allowed to rise to about -20 °C. It was then quenched with water (2 ml) at -50 °C and the ether layer was decanted from the ice. The ice was washed with ether (3 x 15 ml), the ether fractions were combined and methyl acrylate (10 mol.equiv., 1.2 g) was added. The reaction mixture was stirred at room temperature for 3 h after which the crude product was dried ($MgSO_4$) and the volatiles were removed at 14 mm Hg. Column chromatography eluting with petrol and ether (5:1) afforded **methyl 2-bromo-2-(1-bromo-2-methylprop-1-enyl)cyclopropane carboxylate (4f)** (0.28 g, 70 %) ($C_9H_{12}Br^{79}Br^{81}O_2$ requires: 311.9180. Found: 311.9144); the ^1H n.m.r. spectrum (at r.t.) showed the presence of two rotamers in the ratio of ca. 1.7:1. The major rotamer showed δ_H 3.73 (3H, s), 2.47 (1H, t, J 7.9 Hz), 1.88 (3H, s); the minor rotamer showed δ_H 3.68 (3H, s), 2.89 (1H, t, J 8.0 Hz). In addition there were signals at 1.9 - 2.1 (m) and 1.25 (br.s) for the remaining protons in the two rotamers; δ_H (60°C) 3.6 (3H, br.s), 2.2-1.9 (3H, v.br.s), 1.8 (6H, s); a small additional singlet (ca 5 %) was seen at 3.8 in the low and high temperature spectra which might correspond to the methoxy group of a second isomer; g.l.c. also showed the presence of a minor component (ca 2.5 %) at slightly longer retention time than (**4f**); δ_C 168.0, 167.0, 142.0, 140.2, 118.7, 117.0, 52.4, 52.0, 39.3, 37.6, 32.9, 29.7, 27.5, 25.6, 21.9 plus a few minor signals; υ_{max} 2949 s, 1737 s, 1638 s, 1438 s, 653 s; m/z 310/312/314 (M^+).

(b) Methyl 2-bromo-2-(1-bromo-2-methylprop-1-enyl)-1-methylcyclopropanecarboxylate: The reaction in (a) was repeated using methyl methacrylate (10 mol. equiv., 1.3 g) instead of methyl acrylate. Work up as before gave **methyl 2-bromo-2-(1-bromo-2-methyl-prop-1-enyl)-1-methylcyclopropanecarboxylate (4e)** (0.37 g, 88 %) ($C_{10}H_{14}Br^{79}Br^{81}O_2$ requires: 325.9336. Found: 325.9301); δ_H (r.t.) showed the presence of two rotamers in a ca. 1:1 ratio: 3.65 (3H, s), 3.55 (3H, s), 2.44 (1H, d, J 7.3 Hz), 2.35 (1H, d, J 6.8 Hz), 1.97 (3H, s), 1.85 (3H, s), 1.83 (3H, s), 1.73 (3H, s), 1.66 (3H, s), 1.60 (3H, s), 1.39 (1H, d, J 6.8 Hz). The fourth ring H was apparently a doublet at 1.6 but this was partly covered by the methyl signal at 1.66; δ_H (100 °C) 3.7 (3H, br), 2.6 (1H, br), 2.55 (1H, br), 2.0 (1H, br), 1.85 (6H, s), 1.75 (3H, br.s), 1.45 (1H, br.s); δ_C 170.9, 170.7, 139.9, 138.4, 120.6, 120.4, 52.7, 52.1, 49.3, 47.3, 37.8, 34.9, 32.9, 32.6, 25.6, 25.4, 22.1, 20.7, 20.3; υ_{max} 2947 s, 1730 s, 1638 s, 1452 s, 666.2 s.

(c) 1-Cyano-2-bromo-2-(1-bromo-2-methylprop-1-enyl)cyclopropane: The procedure in (a) was repeated using methyllithium (1.5 mol.equiv., 1.5 M, 2.6 ml) and 3,3-dimethyl-1,1,2,2-tetrabromocyclopropane (1.0 g, 0.0026 mol) and ether (10 ml) and adding acrylonitrile (10 mol.equiv., 1.4 g) instead of methyl acrylate. After work up, column chromatography eluting with a mixture of petrol and ether (5:1), gave a major product (0.2 g, 28 %) which was a solid and a minor product (0.06 g, 9 %) which was a brown oil. The major product was (**4g**), m.p. 85-87 °C ($C_8H_9NBr_2$ requires: C 34.41; H 3.25; N 5.02. Found: C 34.90; H 3.26; N 4.80 %) which showed δ_H (at r.t.) 2.58 (ca. 1H, very broad), 2.09 (4H, v.br.), 1.96 (3H, s) on top of 1.9 (1H, v.br); δ_H (at -55 °C) showed the presence of two rotamers in the ratio of ca. 3:2. The major rotamer showed signals at 2.66 (1H, dd, J 7.1, 9.8 Hz), 2.08 (3H, s), 1.92 (3H, s), 1.85 (1H, t, J 7.1 Hz); the signal for the third ring

proton is probably underneath the broad singlet at 2.08. The minor rotamer showed signals at 2.38 (1H, dd, J 6.1, 9.7 Hz), 2.25 (1H, dd, J 6.1, 9.7 Hz), 1.97 (3H, s), 1.90 (3H, s); the signal for the third ring proton is probably obscured by the broad singlet at 1.90; δ_C (r.t.) 117.0, 35 br, 27.8 br, 25.9 br, 22.6 br, 22.0 br; δ_C (at -55 °C) 145.03, 142.6, 117.3, 117.1, 115.3, 35.8, 34.8, 30.1, 27.3, 25.8, 22.8, 22.3, 21.7, 17.3; υ_{max} 2916.4 s, 2244.0 s, 1633 s, 1435.0 s, 711.9 s; m/e 277, 279, 281 (M). The minor product was provisonally characterised as (**6g**) which showed δ_H (at r.t.) 1.94 (3H, s), 1.84 (3H, s), 2.0-1.94 (1H, dd, J 6.4, 9.6 Hz), 1.94-1.89 (1H, t, J 6.4 Hz), 1.88-1.83 (1H, dd, J 3.7, 9.6 Hz); δ_H (at -55°C) 1.92 (3H, s), 1.80 (3H, s), 2.3-2.0 (3H, v.br); δ_C 141.72, 118.4, 117.5, 35.8, 29.1, 25.5, 21.96, 19.1; υ_{max} 3028.5 s, 2916.5 s, 2246.4 s, 1636.2 s, 1434.7 s, 733.2 s; m/z 277, 279, 281 (M).

(d) 1-Acetyl-2-bromo-2-(1-bromo-2-methylprop-1-enyl)cyclopropane: The reaction was repeated as in (a) except that methyl vinyl ketone (10 mol.equiv., 0.91 g) was added instead of methyl acrylate. Work up as before and removal of the volatiles at 14 mm Hg, followed by column chromatography eluting with petrol and ether (5:1), afforded the product, **1-acetyl-2-bromo-2-(1-bromo-2-methylprop-1-enyl)cyclopropane (4h)** (0.13 g, 34 %) ($C_9H_{12}Br_2O$ requires: 295.9231. Found: 295.9195) which showed δ_H 2.77 (1H, t, J 7.3 Hz), 2.42 (3H, br.s0), 2.25 (1H, t, J 6.7 Hz), 2.1-2.0 (1H, m), 1.98 (3H, s), 1.85 (3H, s); in addition there were a number of small signals in the region 1.5 - 2.4 and a broad triplet at 3.1, apparently due to a minor rotamer; δ_C 202, 141, 118, 45, 43, 39.5, 33.0, 30.3, 25.7, 21.9; υ_{max} 2999 s (CH), 2914 s, 1709 s, 1637 s, 1418 s, 676 s.

Conversion of 1-Cyano-2-bromo-2-(1-bromo-2-methylprop-1-enyl)cyclopropane into the ester

Gaseous HCl was bubbled through an ice-cold solution of dry methanol (2 ml) and diethyl ether (3 ml) for 5 mins. The major isomer (see above) of 1-cyano-2-bromo-2-(1-bromo-2-methylprop-1-enyl)cyclopropane (0.2 g, 0.7 mmol) in dry ether (2 ml) was added dropwise to the mixture. The mixture was stirred for 1 h at 0 °C and then stirred overnight at room temperature. Saturated aq. $NaHCO_3$ was then added and the organic layer was separated. The aqueous layer was extracted with ether (3 x 10 ml) and the combined ether layers were dried over $MgSO_4$, filtered and the volatiles removed at 14 mm Hg to give the ester. It was purified by column chromatography eluting with petrol and ether (5:2) (0.04 g, 20 %). The glc, tlc, ^1H and ^{13}C n.m.r. spectra were identical to those of the ester (**4f**) prepared above.

Conversion of 1-Acetyl-2-bromo-2-(1-bromo-2-methylprop-1-enyl)cyclopropane into its Hydrazone

Concentrated sulphuric acid (0.2 ml) was added very cautiously to a suspension of 2,4-dinitrophenylhydrazine (1 mol.equiv., 0.074 g) in methanol (5 ml). The warm suspension was filtered. The cyclopropane (0.11 g, 0.37 mmol) in methanol (1 ml) was added to the warm filtrate, allowed to stand for 30 minutes and then diluted with water (1 ml). The precipitate was filtered, washed with water, dried under vacuum and crystallised from hot ethanol to give (**7**), m.p. 165-166 °C ($C_{15}H_{16}Br_2N_4O_4$ requires: C 37.82; H 3.38; N 11.76 %. Found: C 37.32; H 3.33; N 11.47 %) which showed a broad proton n.m.r. spectrum at room temperature which could be interpreted in terms of signals for two rotamers in the ratio of ca. 1:2; δ_H (at -40 °C) 11.13 (1H, s), 9.17 (1H, d, J 2.5 Hz), 8.30 (1H, dd, J 9.6, 2.5 Hz), 7.6 (1H, d, J 9.6 Hz), 2.53 (1H, dd, J 9.1 Hz), 2.36 (1H, t), 2.28 (3H, s), 2.20 (1H, dd), 2.08 (3H, s), 1.80 (3H, s). There were also signals for the minor rotamer at 11.1 (s), 8.3 (1H, m), 7.9 (1H, d), 7.05 (1H, d. v.small coupling), 3.0 (1H, m), 2.07 (3H, s), 1.79 (3H, s), plus other signals; δ_H (at 60 °C) 10.94 (1H, br.s), 9.08 (1H, d, J 2.5 Hz), 8.22 (1H, br.d, J 7.0 Hz), 7.7 (1H, br.s), 2.12 (3H, s), 1.77 (3H, s), 1.43 (3H, br.s), plus very broad signals between 1.9-2.3.

3-(2-Hydroxyethyl)-3-methyl-1,1,2,2-tetrabromocyclopropane

2-Methoxypropene (36.8 g, 48.9 mol) was added to a stirred solution of 1,1-dibromo-2-methylbut-1-en-4-ol[14] (25 g, 0.1 mol) in ether (50 ml) at 0°C. An exothermic reaction commenced on addition of pyridinum p-tolulenesulphonic acid (0.05 eq). The reaction was stirred for 0.25 h at room temperature, after which TLC showed no starting material was left. The reaction was quenched with a saturated aq. sodium bicarbonate and the aqueous layer was extracted with ether (2 x 50 ml); the organic layers were dried and the solvent was removed at 14 mm Hg to give **1,1-dibromo-2-methylbut-1-en-4-yl-2-methoxyprop-2-yl ether** (30 g, 92.6%).

A mixture of bromoform (13.8 ml), cetrimide (2.5 g) and few drops of triethylamine in dichloromethane (50 ml) was stirred for ca. 10 min, after which the above ether (25 g) was added. Whilst being rapidly stirred, sodium hydroxide (40 g) in water (40 ml) was added slowly and the temperature was maintained below 30 °C. The reaction mixture was stirred at room temperature for 48 h, and then poured into water (20

ml) and extracted with dichloromethane (3 x 100 ml). The solvent was removed at 14 mm Hg and petrol (300 ml) was added to the residue and stirred for 15 min. Cetrimide separated out and was filtered off. The filtrate was dried and evaporated at 14 mm Hg to give the protected cyclopropane alcohol. The crude product was stirred with aqueous methanol in the presence of p-toluenesulphonic acid for 0.25 h, then the clear solution was decanted and concentrated. The residue was washed with water and extracted with ether (3 x 100 ml), the organic layer was dried and the solvent was removed at 14 mm Hg to give a crude solid product (15 g, 70 %), which was columned on silica eluting with petrol and ether (1:1) to give **3-(2-hydroxyethyl)-3-methyl-1,1,2,2-tetrabromo- cyclopropane** (**14**, X = OH) (12 g, 56 %), m.p. 72-74 °C (Found: C 17.42, H 1.84; $C_6H_8OBr_4$ requires C 17.33, H 1.93%) which showed δ_H 1.5 (3H, s), 2.1 (2H, t, J 7.0 Hz), 1.8 (br, s), 3.8 (2H, t, J 7.0 Hz); δ_C 60.0, 49.0, 40.83, 37.8, 22.6; υ_{max} 3600, 1449.1, 1287.9, 1267.3, 832.0 cm^{-1}.

1,1,2,2-Tetrabromo-3-methyl-3-(2-methoxyethyl)cyclopropane

(a) Sodium hydroxide (15 g, 0.36 mol) in water (15 ml) was added carefully to a rapidly stirred solution of 1,1-dibromo-4-methoxy-2-methylbut-1-ene[14] (9.45 g, 0.03 mol) in dichloromethane (50 ml), bromoform (0.07 mol, 6.4 ml) and cetrimide (2 g) at room temperature. The mixture was stirred rapidly for 48 hours. Dichloromethane (300 ml) was then added followed by brine (300 ml) and the product was extracted with further dichloromethane. The combined organic layers were dried and the solvent was removed at 14 mm Hg. The residue was stirred with petrol (250 ml) for 15 min and filtered. The filtrate was dried and the solvent was removed at 14 mm Hg to give a brown oil, which was columned on silica eluting with petrol and ether (5:1) to give **1,1,2,2-tetrabromo-3-methyl-3-(2-methoxyethyl)cyclopropane** (**14**, X = OMe) (6.5 g, 41 %) (Found: M^+ 425.7465. $C_7H_{10}OBr_4$ requires 425.7465) which showed δ_H 1.5 (3H, s), 2.0 (2H, t, J 6.9 Hz), 3.3 (3H, s), 3.5 (2H, t, J 6.9 Hz); δ_C 69.5, 53.9, 49.05, 38.2, 22.96, 20.35); υ_{max} 2926, 1449, 1383, 1116, 761 cm^{-1}.

(b) A mixture of 3-hydroxyethyl-3-methyl-1,1,2,2-tetrabromocyclopropane (2 g, 4.8 mmol) and tetra-n-butylammonium iodide (0.05 g, 0.14 mmol) in dichloromethane (20 ml) was equilibrated by vigorous stirring for 30 min with 50% aq. sodium hydroxide (0.6 g, 0.014 mol). Dimethyl sulphate (0.68 ml, 7.2 mmol) was added dropwise with cooling, then the mixture was stirred for 18 h. Concentrated aqueous ammonia (2 ml) was added and the mixture was stirred for 30 min then poured into water (100 ml). After extracting with dichloromethane (3 x 50 ml) the organic layers were washed with water (50 ml), dried and concentrated under reduced pressure to give 1,1,2,2-tetrabromo-3-methyl-3-(2-methoxyethyl)cyclopropane (1.7 g, 82 %), identical to that in (a).

1,1,2,2-Tetrabromo-3-methyl-3-(2-bromoethyl)cyclopropane

Reaction of 1,1,4-tribromo-2-methylbut-1-ene[14] with bromoform and base as above under phase transfer conditions gave **1,1,2,2-tetrabromo-3-methyl-3-(2-bromoethyl)cyclopropane** (**14**, X = Br), m.p. 74-76 °C (38 %) (Found: C 14.92, H 1.24; $C_6H_7Br_5$ requires C 15.05, H 1.47) which showed δ_H 3.5 (2H, complex signal), 2.36 (2H, complex), 1.52 (3H, s); δ_C 47.8, 41.6, 38.8, 27, 22.2; υ_{max} 760 cm^{-1}.

Preparation of E/Z-1-bromo-2-methylbut-1-en-4-yl 2-methoxyprop-2-yl ether

2-Methoxypropene (17.6 g, 23.4 ml) was added to a stirred solution of E/Z-4-bromo-3-methylbut-3-en-1-ol (8.1 g, 0.04 mol) in ether (50 ml) at 0°C.[18] An exothermic reaction occurred on addition of pyridinium p-toluene sulphonic acid (0.24 g, 0.98 mmol). The reaction was stirred for 0.25 h at room temperature, after which TLC showed no starting material, and then worked up as above to give E/Z-1-bromo-2-methylbut-1-en-4-yl-2-methoxyprop-2-yl ether in ratio 4:1 (10.5 g, 90.6%), which showed (major isomer) 5.9 (1H, q, J 1.2 Hz), 3.4 (2H, t, 6.8 Hz), 3.1 (3H, s), 2.3 (2H, dt, J 0.9, 6.8 Hz), 1.78 (3H, d, J 1.2 Hz), 1.28 (6H, s); (minor isomer) 5.89 (1H, br, s), 3.15 (3H, s), 2.4 (2H, t, J 7.16 Hz), 1.29 (6H, s) (the remaining signals were obscured by those for the major isomer).

Preparation of 3-(2-hydroxyethyl)-3-methyl-1,1,2-tribromocyclopropane

A mixture of bromoform (14.8 ml), cetrimide (2.5 g) and a few drops of triethylamine in dichloromethane (50 ml) was stirred for ca. 10 min, after which E/Z-1-bromomethylbut-1-ene-4-yl-2-methoxyprop-2-yl ether (20 g) was added. While the mixture was rapidly stirred, sodium hydroxide (50 g) in water (50 ml) was added slowly and the temperature was maintained below 30 °C. After stirring at room temperature for 48 h, work up and deprotection as above gave **3-(2-hydroxyethyl)-3-methyl-1,1,2-tribromocyclopropane** (**29**) as a mixture of isomers in ratio 4:1 (16.2 g, 57 %) (Found M^+: 333.8203. $C_6H_9OBr_3$ requires 333.8203), which

showed δ_H (major isomer) 3.85 (2H, m), 3.55 (1H, s), 2.02 (2H, dt, J 3.85, 7.0 Hz), 1.82 (1H, broad, s), 1.36 (3H, s); δ_C 59.8, 42.4, 42.0, 41.0, 38.15, 20.2); (minor) 3.4 (1H, s), 1.9 (2H, m), 1.49 (3H, s); the remaining signals were obscured by the major isomer; δ_C 59.5, 42.1, 41.15, 31.8, 31.44, 22.8; υ_{max} 3354, 1449, 1050, 794, 692.

Preparation of 1,2-dibromo-3-methyl-3-(2-bromoethyl)cyclopropene

Methyllithium (0.62 ml, 0.93 mmol) was added to a stirred solution of 1,1,2,2-tetrabromo-3-(2-bromoethyl)cyclopropane (0.3 g, 0.62 mmol) in dry ether (15 ml) at -78 °C under nitrogen. The mixture was stirred for 5 min before quenching with water at this temperature; work-up as above gave 1,2-dibromo-3-methyl-3-(2-bromoethyl)cyclopropene (**11**, X = Br) (0.16 g, 84%) which showed δ_H 3.2 (2H, t, J 7.3 Hz), 2.1 (2H, t, J 7.3 Hz), 1.19 (3H, s); δ_C 128.9, 111.0, 42.56, 41.3, 29.74, 23.73; υ_{max} 1777, 1446, 1248, 844 cm^{-1}.

Preparation of 1,2-dibromo-3-methyl-3-(2-methoxyethyl)cyclopropene

Methyllithium (1.55 ml, 2.32 mmol) was added to a stirred solution of 1,1,2,2-tetrabromo-3-(2-methoxyethyl)cyclopropane (1.0 g, 2.31 mmol) in dry ether (15 ml) at -78 °C under nitrogen. Work-up as above gave 1,2-dibromo-3-methyl-3-(2-methoxyethyl)-cyclopropene (**11**, X = OMe) (0.5 g, 80%) which showed δ_H 3.23 (3H, s), 3.21 (2H, t, J 6.4 Hz), 1.86 (2H, t, J 6.4 Hz), 1.22 (3H, s); δ_C 108.57, 68.35, 57.57, 40.23, 35.86, 23.08; υ_{max} 1736, 1448, 1118, 738.

Reaction of 1,1,2,2-tetrabromo-3-methyl-3-(2-methoxyethyl)cyclopropane with methyllithium and 2,3-dimethylbut-2-ene

Methyllithium (0.85 ml, 1.3 mmol) was added to a stirred solution of 1,1,2,2-tetrabromo-3-methyl-3-(2-methoxyethyl)cyclopropane (0.5 g, 1.16 mmol) and 2,3-dimethylbut-2-ene in dry ether (10 ml) under nitrogen at -78 °C. The reaction mixture was stirred for 3 h at room temperature and then quenched with water (5 ml), and the ether layer dried ($MgSO_4$) and the solvent removed at 14 mm Hg to give a brown oil, which was columned on silica eluting with petrol and ether (5:1) to give a mixture of two isomers of **4-(1-bromo-2,2,3,3-tetramethylcyclopropyl)-4-bromo-3-methyl-3-butyl methyl ether** in ratio 4:3 (yield: 62.5%) (Found: M^+ 352.0037. $C_{13}H_{22}OBr_2$ requires 352.0037); δ_H 3.54-3.31 (4H, m), 3.3 (3H, s), 3.26 (3H, s), 2.69-2.5 (2H, m), 2.47-2.2 (2H, m), 1.78 (3H, s), 1.74 (3H, s), 1.27 (3H, s), 1.25 (3H, s), 1.16 (6H, s), 1.1 (6H, s), 1.04 (6H, s); δ_C 139.7, 139.2, 125.8, 125.2, 69.7, 69.5, 58.46, 58.3, 38.4, 35.8, 31.56, 31.4, 22.8, 22.6, 22.16, 21.4, 21.15, 20.45, 19.3, 10.04; υ_{max} 2921, 2825, 1622, 1377, 1114, 856 cm^{-1}.

The reaction of 1,1,2,2-tetrabromo-3-methyl-3-(2-bromoethyl)cyclopropane with methyllithium in the presence of 2,3-dimethylbut-2-ene

Reaction as above gave a mixture of two isomers of **3-bromo-3-(1,4-dibromo-2-methyl-butyl-1-enyl)-1,1,2,2-tetramethylcyclopropane** (60.0 %) which was separated by chromatography on silica eluting with petroleum ether. The first isomer (Found: M^+ 399.9037; $C_{12}H_{19}Br_3$ requires 399.904) showed δ_H 3.6-3.45 (2H, m), 2.95 (1H, ddd, J 5.8, 11.3, 1.8 Hz), 2.6 (1H, dt, 54.8, 11.3 Hz), 1.9 (3H, s), 1.38 (3H, s), 1.25 (3H, s), 1.19 (3H, s), 1.13 (3H, s); δ_C 138.90, 127.20, 59.,17, 41.62, 39.66, 36.73, 31.18, 27.74, 22.76, 22.37, 20.56, 20.27; m/z: 320 (M^+ - Br); υ_{max} 2358.0, 1448.2, 1114.5. The second isomer showed δ_H 3.6 - 3.45 (2H, m), 2.9 - 3.1 (1H, m), 2.7 (1H, m), 1.85 (3H, s), 1.34 (3H, s), 1.24 (3H, s), 1.2 (3H, s), 1.17 (3H, s); δ_C 139.1, 127.0, 41.3, 39.66, 31.74, 29.3, 28.0, 22.75, 22.25, 21.1, 20.5, 19.36.

Reaction of 1,1,2,2-tetrabromo-3-methyl-3-(2-hydroxyethyl)cyclopropane with methyllithium

(a) Methyllithium (1.6 ml, 2.52 mmol) was added slowly to a stirred solution of the tetrabromide (0.5 g, 1.2 mmol) in dry ether (10 ml) under nitrogen at -78 °C. Stirring was continued for 3 min before the reaction was quenched with water (3 ml) at -78 °C. The aqueous layer was extracted with ether (5 x 10 ml) and the extracts were dried and the solvent evaporated carefully at 5 °C and 14 mm Hg to give a brown oil; chromatography on silica eluting with petrol gave Z-1,2-dibromo-3-methyl-1,3-butadiene as a colourless oil (0.11 g, 38%) which showed: δ_H 6.9 (1H, s), 5.5 (1H, br.s), 5.2 (1H, br.s), 2.01 (3H, d, J 0.76 Hz); δ_C 140.06, 133.16, 119.91, 109.76, 20.61, identical to an authentic sample.[15]

(b) The above reaction was repeated and quenched with D_2O, to give Z-1,2-dibromo-1-deuterio-3-methyl-1,3-butadiene (40%) which was identical by ^1H NMR except that the signal at δ 6.9 was reduced in size to about 20 % of one proton. The mass spectrum of the product showed about ca. 75 % incorporation of one D.

Reaction of 1,1,2,2-tetrabromo-3-methyl-3-(2-hydroxyethyl)cyclopropane with diethylphosphite and triethylamine

Triethylamine (0.14 g, 1.4 mmol) was added to a stirred solution of the tetrabromide (0.3 g, 0.72 mmol) and diethylphosphite (0.4 g, 2.8 mmol) under argon atmosphere at room temperature. The reaction was stirred at 90 °C for 4.5 h, and then cooled to room temperature and diluted with ether (15 ml), filtered and the solvent evaporated carefully at 0 - 5 °C and 14 mm Hg. The residue was columned on silica eluting with petrol to give Z-1,2-dibromo-3-methyl-1,3-butadiene (0.065 g, 40 %), identical to that obtained above.

Oxidation of 1,1,2,2-tetrabromo-3-methyl-3-(2-hydroxyethyl)cyclopropane

Potassium permanganate (15.1 g, 0.09 mol) in water (100 ml) was stirred rapidly for 16 h with tetrabutyl-ammonium bromide (0.5 g) and 1,1,2,2-tetrabromo-3-methyl-3-(2-hydroxyethyl)cyclopropane (4 g, 9.6 mmol) in benzene (20 ml). The reaction was treated carefully at 0 °C with saturated aq. sodium metabisulphite until the brown coloration was discharged, acidified to pH 1 with dil. sulphuric acid and extracted with ether (3 x 100 ml). The organic layers were dried and the solvent was removed at 14 mm Hg to give a solid (4 g, 97 %), which was crystallised from petrol and ether to give **2-(1,1,2,2-tetrabromo-3-methylcycloprop-3-yl)ethanoic acid** (3.56 g, 86.5 %), m.p. 140-142 °C (Found: C 17.21, H 1.38. $C_6H_6O_2Br_4$ requires C 17.21, H 1.4 %); δ_H 1.7 (3H, s), 3.0 (2H, s); δ_C 156.3, 47.2, 43.1, 36.7, 23.3, 20.3; υ_{max} 3021 (v broad), 1708, 1410, 1229, 760 cm^{-1}.

Oxidation of 1,1,2-tribromo-3-methyl-3-(2-hydroxyethyl)cyclopropane

Oxidiation of (**29**) as above gave **(1,1,2-tribromo-3-methyl-3-cyclopropyl)ethanoic acid (30)** (1.9 g, 60 %), m.p. 104-106 °C (Found: C 20.68, H 1.93. $C_6H_7O_2Br_3$ requires: C 20.51, H 1.99 %); δ_H 3.64 (1H, s), 2.9 (1H, d, J 17 Hz), 2.8 (1H, d, J 17 Hz), 1.49 (3H, s); δ_C 175.8, 43, 41.2, 40.5, 30.6, 20.4; υ_{max} 2933 (v.br), 1705, 1412, 1268, 1229, 908, 820 cm^{-1}.

Reaction of (1,1,2,2-tetrabromo-3-methyl-3-cyclopropyl)ethanoic acid with mercuric oxide and bromine

Bromine (0.2 g, 1.28 mmol) in carbon tetrachloride (5 ml) was added dropwise to a stirred suspension of the acid (0.5 g, 1.16 mmol) and red mercuric oxide (0.27 g, 1.2 mmol) in carbon tetrachloride (15 ml) at 85 °C. The mixture was refluxed for 3 h, stirred at room temperature for 12 h, treated with petrol (20 ml), stirred for 5 min and filtered through flash silica. The filtrate was evaporated at 14 mm Hg and the residue was columned on silica eluting with petrol to give **1,1,2,3,4-pentabromo-3-methyl-1-butene** (0.35 g, 65 %), which showed δ_H 4.87 (1H, dq, J 1.1, 10.3 Hz), 3.70 (1H, d, J 10.3 Hz), 2.44 (3H, d, J 1.1 Hz); δ_C 129.1, 93.3, 61.6, 42.3, 40.65; υ_{max} 1523, 1443, 1228, 1080, 1036, 855, 778, 700 cm^{-1}; m/z: 460/462/464/466 /468/470 (M^+).

Reaction of (1,1,2-tribromo-3-methyl-3-cyclopropyl)ethanoic acid with mercuric oxide and bromine

Reaction as above using bromine (0.25 g, 1.5 mmol) in carbon tetrachloride (5 ml) and the acid (0.5 g, 1.4 mmol) and red mercuric oxide (0.34 g, 1.5 mmol) in carbon tetrachloride (15 ml) gave 1,1,3,4-tetrabromo-3-methyl-1-butene (**31**) (0.15 g, 27 %), which showed δ_H 6.8 (1H, s), 4.3 (1H, d, J 10.1 Hz), 3.78 (1H, d, J 10.1 Hz), 2.1 (3H, s); δ_C 138.84, 95.3, 59.3, 41.9, 30.46; υ_{max} 1602, 1037, 864, 816, 775 cm^{-1}; m/z 302/304 /306/308 (M^+-Br).

Reaction of 1,1,2,3,4-Pentabromo-3-methylbut-1-ene with diethylphosphite and triethylamine

Triethylamine (0.02 ml, 0.215 mmol) was added to a stirred solution of 1,1,2,3,4-pentabromo-3-methylbut-1-ene (0.1 g, 0.21 mol) and diethylphosphite (0.1 ml, 0.86 mmol) at 5 °C. The mixture was allowed to reach 20 °C, stirred for 30 min, and then columned directly on silica, eluting with petrol to give a colourless oil, 1,3,4-tribromo-3-methyl-1-butyne (**25**) (0.025 g, 38 %) which showed δ_H 4.01 (1H, d, J 10.1 Hz), 3.8 (1H, d, J 10.1 Hz), 2.12 (3H, s); δ_C 93.31, 79.7, 42.0, 36.64, 32.11; υ_{max} 2205, 1037 cm^{-1}; m/z 302/304/306/308 (M^+).

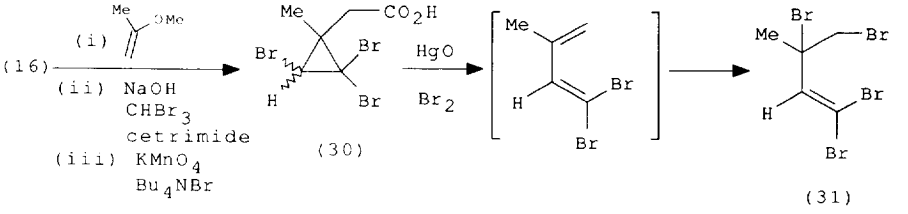
Reaction of 1,1,2,3,4-pentabromo-3-methylbut-1-ene with 1,8-Diazabicyclo[5.4.0]undec-7-ene

1,8-Diazabicyclo[5.4.0]undec-7-ene (0.4 ml, 2.6 mmol) was stirred for 30 min with 1,1,2,3,4-pentabromo-3-methyl-1-butene (0.5 g, 1.07 mmol) in dry benzene (5 ml) at 20 °C. After 5 min a precipitate had formed. After addition of 5 % HCl (10 ml) and ether (15 ml) and extraction of the aqueous layer with ether (2 x 10 ml), the combined ether layers were washed with water (10 ml), dried, and the solvent removed

at 14 mm Hg to give an oil which was one spot by TLC. This was further purified by column on silica eluting with petrol to give 1,1,2,4-tetrabromo-3-methylbuta-1,3-diene (**26**) (0.37 g, 90 %) which showed δ_H 6.4 (1H, q, J 1.2 Hz), 1.9 (3H, d, J 1.24 Hz); δ_C 139.83, 124.69, 119.19, 112.54, 17.95; υ_{max} 1611.3, 1280.2 cm^{-1}; m/z 380/382/384/386/388 (M^+), 301/303/305/307 (M^+-Br).

* Compound (**24**) was debrominated by reaction with diethyl phosphite and triethylamine to give (**25**) (38 %) while dehydrobromination with diazabicyclo[5.3.0]undec-7-ene gave the tetrabromide (**26**) (90 %).

** In the same way, the tetrabromide (**31**) (27 %) was obtained from (**30**).



\# We wish to thank the SERC Crystallography Service in Cardiff for carrying out this structure determination, the details of which will appear elsewhere.

\## An excess of methyl lithium should be avoided as (11, X = Br, OMe) react further with methyl lithium at 0 - 20 C to generate 5-bromo- or 5-methoxy-3-methylpenta-1,2-dienylidene. A full account of the formation of such allenic carbenes will be presented elsewhere.

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