1,2-Dibromoalk-2-enylidenes by Ring-opening of 1,2-Dibromo-3-alkylcyclopropenes at Ambient Temperature

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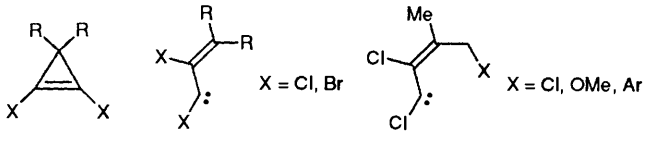
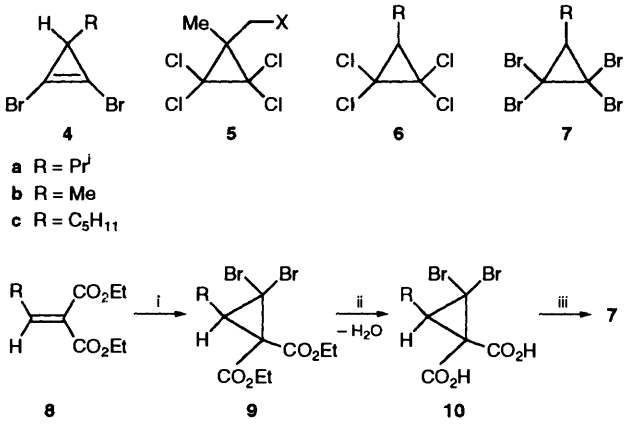
1,2-Dibromo-3-alkylcyclopropenes have been obtained by 1,2-debromination of 1,1,2,2-tetrabromocyclopropanes by reaction with 1 mol equiv. of methyllithium. They ring-open at ambient temperature and, in the presence of an electron-rich or electron-poor alkene, a cyclopropane is formed by apparent addition of an intermediate vinylcarbene; addition to (*E*)- and (*Z*)-but-2-enes occurs with retention of alkene relative stereochemistry, indicating that, in this case at least, the carbene is trapped as a singlet.

It is well known that one route to cyclopropenes is ring-closure of a vinylcarbene-like intermediate.[1] Moreover, a number of cyclopropenes are known to undergo the reverse ring-opening process when heated to 150–180 °C,[2] and in some cases the reaction has been shown to be reversible.[3] In a number of specific cases, the ring-opening occurs at much lower temperature;[4,5] we have shown that a range of 1,2-dihalogeno-3,3-dialkylcyclopropenes **1** ring-open at 0–20 °C, and that the derived 1,2-dichloro- or 1,2-bromo-chloro-vinylcarbenes **2** can be trapped, *e.g.*, by addition to electron-rich and electron-poor alkenes,[6,7] by addition to alkynes and phosphaalkynes[8] and by insertion into the C–H bond α to oxygen in ethers. When the two 3-substituents are different, the reaction often leads to the trapping of only one stereoisomer of the presumed planar singlet vinylcarbene, that in which the substituent carrying a heteroatom or an aryl-substituent is *cis* to the carbene centre, *e.g.* **3**.[9,10,11]



1 **2** **3**

We now report the preparation and ring-opening of three 1,2-dibromo-3-alkylcyclopropenes **4** (see Scheme 1).[12] The cyclopropenes **1** have been conveniently prepared by 1,2-dehalogenation of the corresponding tetrahalides, *e.g.* **5** (X = Cl) with methyllithium. The application of this method to the preparation of cyclopropenes **4** required the corresponding halides **6** or **7** (Scheme 1). Preliminary experiments showed that the addition of dichlorocarbene to 1,1-dichloroprop-1-ene did not occur in high yield. The carbene was generated from the thermolysis of sodium trichloroacetate in dimethoxyethane, from chloroform and base under phase transfer conditions, or from the thermolysis of phenyl trichloromethylmercury; the highest yield, obtained in the last case, was only 27%. When the last two methods were repeated using 1,1-dichlorohept-1-ene, none of the required cyclopropane was isolated. Reaction of 1,1-dibromo-3-methylbut-1-ene with bromoform and base under phase transfer conditions for 96 h at 20 °C also failed to lead to the required tetrabromocyclopropane. With this in mind, an alternative route to 3-alkyl-1,1,2,2-tetrabromocyclopropanes was developed. Reaction of the alkylidenemalonates **8a–c** with bromoform and aq. sodium hydroxide in the presence of cetrimide (hexadecyltrimethylammonium bromide) or TEBA (benzyltriethylammonium chloride) as a phase transfer catalyst led to the cyclopropanes **9a–c**[13] in very rapid

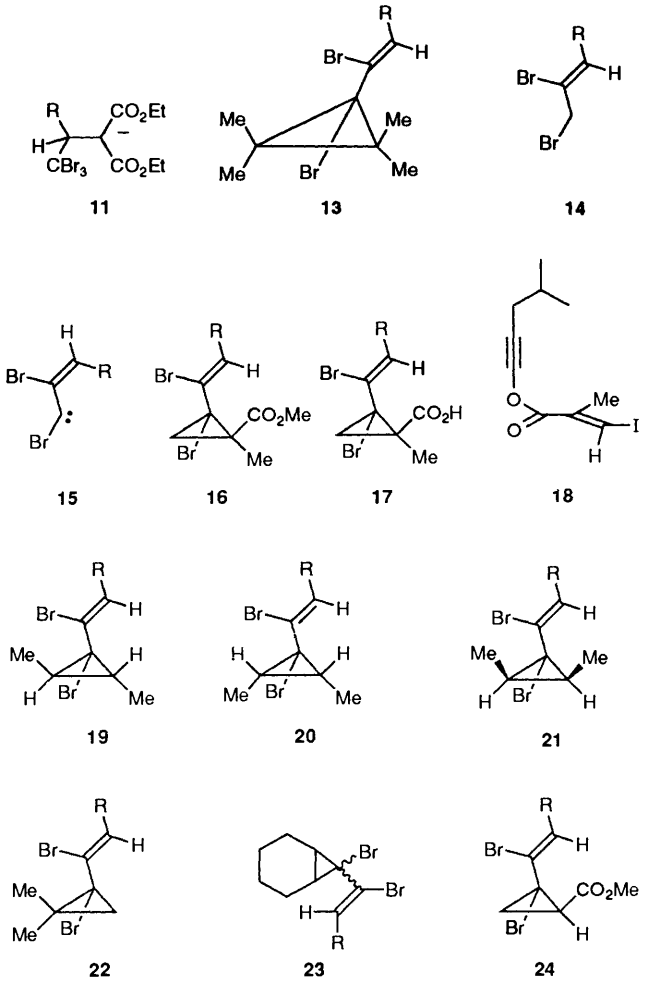


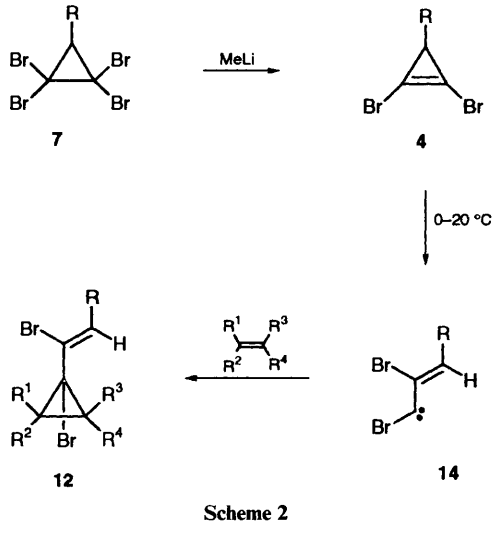
Scheme 1 *Reagents and conditions:* i, $CHBr_3$, aq. NaOH, catalyst; ii, NaOEt, EtOH; iii, HgO, Br_2

reactions which were monitored by NMR and stopped as soon as the starting material had been consumed (see Scheme 1). If the reactions were allowed to proceed for longer periods, the esters **9** underwent hydrolysis to the corresponding dicarboxylic acids **10** which were generally extremely difficult to isolate from the reaction mixture, although **10a** was successfully isolated in this way. The formation of compounds **9** in such rapid reactions may well be explained if they are occurring by Michael-type addition of the tribromomethyl anion to the electron-poor alkene to give **11**, followed by subsequent cyclisation, rather than by carbene addition.[13] Careful hydrolysis of **9a–c** with sodium ethoxide in ethanol–water followed by acidification with a minimum of conc. hydrochloric acid led to the diacids **10a–c**.

The dicarboxylic acids were bromodecarboxylated to the corresponding tetrabromides **7a–c** by reaction with red mercuric oxide and bromine in refluxing carbon tetrachloride.[14,15] Lower yields were obtained if the reaction was carried out in refluxing dichloromethane, or when the diacid **10a** in dichloromethane was irradiated with a tungsten lamp in the presence of lead tetraacetate and bromine.[16] The tetrabromides each showed a characteristic signal at δ_C 39–41 in their ^{13}C NMR spectra for the carbons bearing bromine.[17]

Treatment of **7a** with 1.1 mol equiv. of methyllithium in ether at −78 °C, allowing the reaction mixture to reach room temperature for 30 min, and then quenching with water at low temperature gave the 1,2-dibromocyclopropene **4a** (70%), contaminated with a small amount of ether. The cyclopropene showed a doublet at δ 2.49 (J 4.2) for the ring proton, as well as the signals of the isopropyl group as a 1 H double septet and a 6 H doublet. The cyclopropene was relatively unstable,





Scheme 2

rearranging when stored as a solution in deuteriochloroform for 16 h at 20 °C to give 1,3-dibromo-4-methylpentyne; similar rearrangements have been reported for related 1-halogenocyclopropanes.[6,9] If, however, the ethereal solution of cyclopropene obtained from the debromination with methyllithium was treated with 2,3-dimethylbut-2-ene and set aside for 40 min at 20 °C, the cyclopropane **13a** was isolated (68%); this was characterised on the basis of its ^{1}H NMR spectrum at 263 K which showed a single alkene hydrogen as a quartet at δ 5.69, an isopropyl group at 2.65 (1 H) and 0.98 (6 H), and four methyl singlets at 1.33, 1.21, 1.18 and 1.11. The four ring methyl groups are inequivalent because the preferred conformation of such vinylcyclopropanes has the alkene on C-3 twisted so that it is almost parallel to the C(1)–C(2) bond and rotation is slow on the NMR timescale.[18] At higher temperatures, the spectrum became very broad; this can be explained in terms of interconversion of the rotamers. This product may be explained in terms of ring-opening of the cyclopropene **4a** to the vinylcarbene **14a**, and trapping of this by the alkene. The stereochemistry about the alkene in **13a**, and hence of the trapped carbene, was assigned by analogy with that of a product described below, the structure of which was determined by X-ray crystallography.[12] There was no evidence for the formation of a second isomer derived by trapping of the isomeric carbene **15a**. When the above reaction was repeated using methyl methacrylate in place of 2,3-dimethylbut-2-ene, the product was the ester **16a** (70%). This was converted into the crystalline acid **17a** (70%) by treatment with trimethylsilyl iodide for 75 min at 80 °C in the dark; the structure of this acid was determined by X-ray crystallography, and has been described before.[12] A minor non-acidic product was also isolated; the yield of this could be increased to 29% if the reaction of the ester with trimethylsilyl iodide was carried out at 60 °C. This product was provisionally characterised as the alkyne **18**. The ^{1}H NMR spectrum included an alkene singlet at lowfield, δ 7.27, a 2 H doublet at 2.49, a 1 H multiplet at 2.05, a 3 H singlet at 1.97, and a 6 H doublet at 0.93. The ^{13}C NMR spectrum included a carbonyl carbon at δ 152, two olefinic carbons and two signals at 90.3 and 47.2, assigned to the alkyne; the IR spectrum included peaks at 1750 and 1613 cm^{-1}.

Treatment of the tetrabromide **7a** with 1 mol equiv. of methyllithium, quenching with water, and then addition of other alkenes also led to cyclopropanes (**16a**, **19a–24a**) derived by trapping of the carbene (**14a**) (see Table 1), In the case of addition to *trans*-but-2-ene, a single product, **19a**, was isolated; with *cis*-but-2-ene, two isomers, **20a** and **21a**, were obtained, but GLC showed no evidence for the formation of **19a**. This behaviour is characteristic of a singlet carbene undergoing concerted cheletropic addition to the alkenes,[19] and is summarised in Scheme 2.

In the same way, when the cyclopropanes **7b, c** were allowed to react with 1 mol equiv. of methyllithium at low temperature and the reaction mixtures were warmed to ambient temperature, quenched with water and, in each case, the product in ether was stored in the presence of an alkene for 3–24 h at ambient temperature, the cyclopropanes derived by trapping of the corresponding carbenes **14b, c** were formed. In each case, the addition to *trans*-but-2-ene gave a single product which was different from the two isomers obtained with *cis*-but-2-ene, in agreement with the formation and trapping of a singlet carbene. The stereochemistry about the alkene in the derived vinylcyclopropanes was assigned by analogy to that observed above for **16a**.

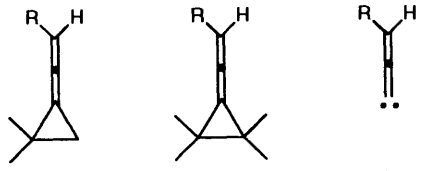
The trapping of the carbenes **14a–c** rather than **15a–c** may be explained in terms of reduced steric hindrance in that form, but is in sharp contrast to the trapping of the apparently more hindered carbene in the case of compounds **1** bearing a heteroatom or an aryl group, when the carbene **3** is trapped preferentially. This latter effect has been explained in terms of stereoelectronic control in the ring opening with such substituents.[20]

Although the above reactions of **7a–c** with 1.1 mol equiv. of methyllithium do lead efficiently to cyclopropenes **4a–c**, it is important to note that in the presence of 2.3 mol equiv. of methyllithium and either 2-methylpropene or 2,3-dimethylbut-2-ene, compounds **7a–c** are instead converted into allenes, e.g. **25** or **26**. These may be derived either by initial formation of dibromides **22a–c** or **13a–c** as above and reaction of these with

Table 1 Preparation of 1-bromo-1-(2-bromoalkenyl)cyclopropanes

Tetrabromocyclopropane	Alkene used	Product	Yield (%)
R = Methyl	Methyl acrylate	**24b**	42.5
	Methyl methacrylate	**16b**	41
	Isobutylene	**22b**	55
	cis-Butene	**20b/21b**	55.6
	trans-Butene	**19b**	52
	Cyclohexene	**23b**	38
	2,3-Dimethylbut-2-ene	**13b**	60
R = Pentyl	Methyl acrylate	**24c**	44
	Isobutylene	**22c**	44
	cis-Butene	**20c/21c**	66
	trans-Butene	**19c**	44
	2,3-Dimethylbut-2-ene	**13c**	54
R = Isopropyl	Methyl acrylate	**24a**	33
	trans-Butene	**19a**	45
	cis-Butene	**20a/21a**	42
	2,3-Dimethylbut-2-ene	**13a**	68
	Methyl methacrylate	**16a**	70

an excess of methyllithium, or by further reaction of an initially formed dibromide **4a–c** with methyllithium to give an allenic carbene **27** which is trapped by the alkene. Similar reactions leading to alkenylidenecyclopropanes have been reported in the reaction of 1,1,2,2-tetrabromo-3,3-dimethylcyclopropane with an excess of methyllithium in the presence of an alkene.[21] A full account of this work, which represents an efficient and flexible route to trisubstituted alk-1-enylidenecyclopropanes, will be presented separately.



25 **26** **27**

Experimental

General Experimental Details.—Reagents were obtained from commercial suppliers and were used without further purification unless otherwise stated. Dichloromethane was distilled over calcium hydride. Diethyl ether and tetrahydrofuran were distilled over sodium wire. Methanol and ethanol were purified and dried by distillation from magnesium turnings containing iodine. Light petroleum was of two types, either of b.p. 40–60 or 60–80 °C. Both were purified by distillation. Ethyl acetate was distilled before use. Unless otherwise stated, all new compounds were homogeneous by either gas liquid chromatography (GLC) or by thin layer chromatography (TLC). GLC was conducted using a Perkin-Elmer Model F17 F.I.D. on a capillary column (30 m × 0.32 mm i.d. Phase, DB5 split ratio of 50:1). The carrier gas was hydrogen (30 cm^3 min^{-1}). TLC was performed using Aldrich silica plates coated with silica gel 60 (F254). Compounds were visualised by examination under a UV source, exposure to iodine vapour or by contact with dodecylmolybdophosphoric acid solution (5% in 95:5 ethanol–water) followed by heating to 180 °C. Column chromatography was conducted with Merck 7736 silica gel under medium pressure. Melting points are uncorrected. IR spectra were obtained as KBr discs (solids) or as liquid films on a Perkin-Elmer 1600 FTIR spectrometer. The mass spectra were obtained using a Finnigan Mat 1020 spectrometer or using the SERC mass spectrometry service in Swansea. Mass measurements reported are where Br refers to ^{79}Br and Cl to ^{35}Cl isotopes unless otherwise stated. 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 at 62.5 MHz for carbons. *J*-Values are quoted in Hz.

Reactions requiring anhydrous conditions were performed using oven-dried glassware (250 °C) that had been cooled under a stream of either dry nitrogen or argon and the experiments were conducted under a positive atmosphere of one of these gases. All yields quoted are for the purified compounds unless otherwise stated. Solids were purified by either recrystallisation or chromatography while liquids and oils were purified either by chromatography or by distillation. The term 'dried' refers to the storage of a solution of the compound over anhydrous magnesium sulfate for a few minutes. Ether refers to diethyl ether.

Reactions of 1,1-Dichloropropene.—With chloroform and base under phase transfer conditions. Sodium hydroxide (9.0 g) in water (9 cm^3) was added to a rapidly stirred solution of 1,1-dichloropropene (5 g, 45 mmol) and cetrimide (0.2 g) in chloroform (15 cm^3). The reaction mixture was stirred rapidly for 24 h at room temperature and then diluted with water and the product extracted with ether (3 × 20 cm^3). The combined extracts were washed with water, dried and evaporated to yield a clear oil which was purified by distillation at 18 °C/0.2 mmHg and characterised as *1,1,2,2-tetrachloro-3-methylcyclopropane* **6** (R = Me) (1.2 g, 14%) (Found: M^+, 191.9053. $C_4H_4Cl_4$ requires *M*, 191.9068); δ_H 2.16 (1 H, q, *J* 6.51) and 1.35 (3 H, d, *J* 6.51); δ_C 67.8, 40.35 and 11.21; *m/z* 192, 178 and 156.

With sodium trichloroacetate. Dry sodium trichloroacetate (8.83 g, 43 mmol) was added to a solution of 1,1-dichloropropene (5.0 g, 43 mmol) in 1,2-dimethoxyethane (10 cm^3). The solution was refluxed for 6 h before a second equiv. of sodium trichloroacetate was added; a further 2 equiv. were added after 8 and then 10 h, respectively, along with 1,2-dimethoxyethane (20 cm^3). After a total of 30 h, the reaction mixture was extracted with ether (3 × 40 cm^3) and the combined extracts were washed with water (2 × 20 cm^3), dried and evaporated. The crude product was purified by Kugelrohr distillation (20 °C/0.2 mmHg) and identified as 1,1,2,2-tetrachloro-3-methylcyclopropane **6** (R = Me) (2.1 g, 24%). All spectral data were identical with those described above.

With phenyl(trichloromethyl)mercury. Phenyl(trichloromethyl)mercury (2.0 g, 5.16 mmol) was added to a solution of 1,1-dichloropropene (0.5 g, 4.3 mmol) in benzene (10 cm^3). The solution was then refluxed for 18 h before it was cooled and filtered. The filtrate was washed with water (5 cm^3) and the

aqueous layer extracted with ether (3 × 5 cm^3). The combined extracts were dried and evaporated to leave a clear oil which was purified by distillation (20 °C/0.2 mmHg) and identified as 1,1,2,2-*tetrachloro*-3-*methylcyclopropane* **6** (R = Me) (0.23 g, 27%). All spectra data were identical with those described above.

Preparation of 1,1-*Dichlorohept*-1-*ene*.—Hexamethylphosphorous triamide (6.3 g, 0.1 mol) in dichloromethane (80 cm^3) was slowly added to hexanal (5 g, 0.05 mol) and bromotrichloromethane (4.92 cm^3, 0.05 mol) in dichloromethane (30 cm^3) at −20 to −10 °C. The reaction mixture was stirred at this temperature until no aldehyde could be detected by TLC, and was then diluted with hexane (40 cm^3), washed with water (2 × 30 cm^3), 10% hydrochloric acid (20 cm^3), and again with water (20 cm^3). The organic layer was dried and the solvent removed by distillation under reduced pressure (30 °C/0.2 mmHg) to give a pale yellow oil (5.1 g, 62%) identified as 1,1-*dichlorohept*-1-*ene*;[22] δ_H 5.8 (1 H, t, *J* 8.2), 2.17 (2 H, m), 1.3 (6 H, complex multiplet) and 0.89 (3 H, t, *J* 6); δ_C 130.0, 120.7, 31.3, 29.1, 27.7, 20.5 and 13.9; *m/z* 165, 137, 130, 123 and 109; ν_{max}/cm^{-1} 2931, 2856, 1751 and 1465.

Reactions of 1,1-*Dichlorohept*-1-*ene*.—*With chloroform and base under phase transfer conditions.* Sodium hydroxide (2.4 g) in water (3 cm^3) was added to a rapidly stirred solution of 1,1-dichlorohept-1-ene (1.4 g, 8.4 mmol) and cetrimide (250 mg) in chloroform (5 cm^3). The solution was stirred vigorously at room temperature for 24 h, after which NMR analysis showed that the starting material was not reacting. The mixture was then warmed to 50 °C. GLC showed that starting material was being consumed but showed no emergence of product at higher retention time. After 7 days, when no starting material could be detected, the reaction mixture was cooled, diluted with water (5 cm^3) and extracted with dichloromethane (3 × 10 cm^3). The combined extracts were dried and evaporated. The TLC and NMR were extremely complex, the latter showing no signals consistent with those of the required product. The complex mixture was not investigated further.

With phenyl(trichloromethyl)mercury. A solution of 1,1-dichlorohept-1-ene (1 g, 6.02 mmol) and phenyl(trichloromethyl)-mercury (2.93 g, 6.02 mmol) in benzene (10 cm^3) was refluxed for 24 h under an inert atmosphere and then allowed to cool. The solid was filtered off and washed with ether (20 cm^3) and the filtrate was washed with water (2 × 5 cm^3). The aqueous layer was extracted with ether and the combined extracts were dried and evaporated. The crude mixture was purified by column chromatography eluting with light petroleum and ether. A single fast running compound was isolated, though NMR revealed this was not the required compound. On further elution of the column, only starting material (0.23 g, 23%) and a complex mixture of products was obtained.

Preparation of 1,1-*Dibromo*-3-*methylbut*-1-*ene*.—A mixture of carbon tetrabromide (9.22 g, 28 mmol), triphenylphosphine (7.3 g, 28 mmol) and zinc dust (1.86 g, 28 mmol) in dichloromethane (30 cm^3) was stirred at room temperature for 30 h. Isobutyraldehyde (1 g, 14 mmol) was added to the mixture which was then stirred for a further 3 h. The reaction mixture was diluted with light petroleum (100 cm^3) and the precipitated material filtered off. The filtrate was evaporated and the insoluble material reworked by additional cycles of dichloromethane extraction and light petroleum precipitation to extract the product. Distillation (54 °C/0.5 mmHg) afforded 1,1-*dibromo*-3-*methylbut*-1-*ene*[23] (1.6 g, 50.5%) (Found: M^+, 225.8994. $C_5H_8Br_2$ requires *M*, 225.8998); δ_H 6.02 (1 H, d, *J* 10), 2.6 (1 H, dq, *J* 10, 8) and 1.1 (6 H, d, *J* 8); δ_C 144.8, 86.9, 33.0 and 21.2; ν_{max}/cm^{-1} 2925, 2868, 1608 and 1464; *m/z* 226, 211, 147 and 132.

Reaction of 1,1-*Dibromo*-3-*methylbut*-1-*ene with Bromoform and Base under Phase Transfer Conditions.*—Sodium hydroxide (0.43 g) in water (1 cm^3) was added to a rapidly stirred solution of 1,1-dibromo-3-methylbutene (0.5 g, 2.19 mmol) and cetrimide (0.2 g) in bromoform (5 cm^3) and the reaction mixture was stirred rapidly for 96 h at room temperature. Work-up gave a compound shown by NMR and TLC to be 1,1-dibromo-3-methylbut-1-ene (0.47 g, 94%).

Reaction of Diethyl Isobutylidenemalonate with Bromoform and Base under Phase Transfer Conditions.—(*a*) Sodium hydroxide (17.6 g) in water (20 cm^3) was carefully added to a rapidly stirred solution of diethyl isobutylidenemalonate[24] (9.5 g, 44 mmol) and TEBA (0.75 g) in bromoform (33 g, 132 mmol). The reaction was stirred for 72 h at 20 °C, when TLC and NMR showed that no starting material remained. After acidification with a minimum volume of conc. HCl, the product was extracted with methanol–chloroform (3 × 50 cm^3); the combined extracts were dried and evaporated to leave a yellow intractable gum. This was stirred with dichloromethane to give a yellow solution and a white solid which was filtered off. Recrystallisation of the solid from methanol gave 2,2-*dibromo*-3-*isopropylcyclopropane*-1,1-*dicarboxylic acid* **10a** (4.1 g, 28%) (Found: C, 29.4; H, 3.0. $C_8H_{10}Br_2O_4$ requires C, 29.1; H, 3.05%); $\delta_H(CD_3OD)$ 5.6 (2 H, br s), 2.31 (1 H, d, *J* 10.63), 1.91 (1 H, m), 1.38 (3 H, d, *J* 6.5) and 1.29 (3 H, d, *J* 6.5); $\delta_C(CD_3OD)$ 168.8, 167.0, 48.9, 47.1, 30.83, 30.43, 21.6 and 21.4; $\nu_{max}(KBr)/cm^{-1}$ 2970, 1709, 1469 and 1408.

The dichloromethane solution was evaporated to leave an amber oil which was identified as *diethyl* 2,2-*dibromo*-3-*isopropylcyclopropane*-1,1-*dicarboxylate* **9a** (3.8 g, 21%) (Found: C, 37.4; H, 4.85. $C_{12}H_{18}Br_2O_4$ requires C, 37.33; H, 4.7%); δ_H 4.25 (2 H, q, *J* 6.8), 4.21 (2 H, q, *J* 6.8), 2.17 (1 H, d, *J* 10.7), 1.63 (1 H, m), 1.29 (3 H, t, *J* 6.8), 1.27 (3 H, t, *J* 6.8), 1.16 (3 H, d, *J* 6.6) and 1.05 (3 H, d, *J* 6.6); δ_C 165.4, 163.5, 62.7, 61.9, 47.4, 44.8, 29.6, 28.9, 20.7, 20.58, 14.02 and 13.95; ν_{max}(film)/cm^{-1} 2965.5, 2871.5, 1737.8, 1464 and 1367; *m/z* 386, 343, 315, 305, 285, 233 and 213.

(*b*) Sodium hydroxide (10 equiv., 22.05 g) in water (22 cm^3) was added carefully to a rapidly stirred solution of diethyl isobutylidenemalonate (11.8 g, 0.055 mol) in CH_2Cl_2 (30 cm^3), bromoform (1.5 equiv., 7.23 cm^3) and TEBA (1.6 g) at 0–5 °C. The solution was stirred rapidly for 15 min, whilst the temperature was maintained < 30 °C by means of an ice–water bath. The ice bath was removed and the reaction mixture was stirred for a further 20 min. The mixture was again cooled to about 10 °C before it was diluted with water (200 cm^3) and extracted with dichloromethane (3 × 50 cm^3). The combined extracts were dried and evaporated at 14 mmHg. Ether (80 cm^3) was added to the crude product which was then stirred for 15 min. The suspension was filtered to remove the TEBA and the filtrate was dried and evaporated at 0.5 mmHg to afford the crude product. Column chromatography of this with light petroleum–ether (5:1) as eluent afforded compound **9a** (30%), identical with that described above.

Reaction of Diethyl Hexylidenemalonate with Bromoform and Base under Phase Transfer Conditions.—To a rapidly stirred solution of diethyl hexylidenemalonate[25] (2.0 g, 8.2 mmol), bromoform (2 cm^3, 25 mmol) and TEBA (250 mg) in dichloromethane (2 cm^3) was added sodium hydroxide (1.6 g) in water (2 cm^3). The reaction mixture was stirred rapidly whilst it was both maintained < 30 °C by means of an ice–water bath and monitored by 60 MHz NMR spectroscopy; after 17 min, it was diluted with water and extracted with dichloromethane (3 × 15 cm^3). The combined extracts were dried and evaporated to leave a pale yellow waxy oil identified as *diethyl* 2,2-*dibromo*-3-*pentylcyclopropane*-1,1-*dicarboxylate* **9c** (2.1 g,

62%) (Found: C, 40.4; H, 5.3. $C_{14}H_{22}Br_2O_4$ requires C, 40.61; H, 5.35%); δ_H 4.2 (4 H, 2 overlapping q), 2.34 (1 H, br t), 1.48 (4 H, br), 1.26 (10 H, 2 overlapping 3 H t on a m) and 0.85 (3 H, br m); δ_C 165.0, 163.8, 61.3, 60.9, 44.3, 36.2, 28.9, 28.6, 28.3, 27.2, 22.2, 13.7 and 13.4; ν_{max}/cm^{-1} 2930, 1740 and 1465; *m/z* 412, 385, 369, 341 and 333.

Reaction of Diethyl Ethylidenemalonate with Bromoform under Phase Transfer Conditions.—Sodium hydroxide (10.75 g) in water (12 cm^3) was added to a rapidly stirred solution of diethyl ethylidenemalonate (5 g, 27 mmol), bromoform (4.6 cm^3, 54 mmol) and TEBA (0.2 g). The solution was stirred rapidly for 10 min whilst its temperature was maintained < 30 °C by means of an ice–water bath. NMR showed that no further olefin remained; the reaction mixture was diluted with water (5 cm^3) and extracted with ether (3 × 15 cm^3). The combined extracts were washed with water (5 cm^3), dried and evaporated to leave an oil which was identified as *diethyl* 2,2-*dibromo*-3-*methylcyclopropane*-1,1-*dicarboxylate* **9b** (8.0 g, 83%) (Found: C, 33.5; H, 3.9. $C_{10}H_{14}Br_2O_4$ requires C, 33.55; H, 3.94%); δ_H 4.25 (2 H, q, *J* 7.1), 4.23 (2 H, q, *J* 7.1), 2.52 (1 H, q, *J* 6.7) and 1.29 (9 H, complex m); δ_C 164.8, 162.8, 62.6, 61.7, 60.8, 44.3, 35.0, 31.5, 13.8 and 12.9; ν_{max}/cm^{-1} 2984 and 1716.

Hydrolysis of Diethyl 2,2-*Dibromo*-3-*isopropylcyclopropane*-1,1-*dicarboxylate.*—Sodium metal (3.12 g, 0.135 mol) was added to absolute ethanol (50 cm^3) and the mixture stirred until most of the sodium had dissolved. It was then refluxed until complete dissolution had taken place. When the solution had cooled, the dicarboxylate (6.3 g, 0.02 mol) and water (1.5 cm^3) were added to it and the mixture was refluxed for 1 h. Evaporation of the solvent at 0.6 mmHg afforded a muddy coloured solid which was treated with ether (70 cm^3) and stirred for *ca.* 15 min. The suspension was allowed to settle and the ether layer was decanted. The product was extracted from the solid by addition of ether (250 cm^3) followed by neutralisation using conc. HCl. The extraction was repeated once and the combined ether layers were dried and evaporated to give 2,2-*dibromo*-3-*isopropylcyclopropane*-1,1-*dicarboxylic acid* **10a** (3.1 g, 58%) (Found: C, 29.4; H, 3.0. $C_8H_{10}Br_2O_4$ requires C, 29.1; H, 3.05%), identical with that described above.

Hydrolysis of Diethyl 2,2-*Dibromo*-3-*methylcyclopropane*-1,1-*dicarboxylate.*—Sodium metal (3.12 g, 0.135 mol) was added to absolute ethanol (50 cm^3) and the mixture stirred until most of the sodium had dissolved; it was then refluxed until complete dissolution had taken place. When the solution had cooled, the ester (0.02 mol) and water (1.5 cm^3) were added to it and the mixture was refluxed for 1 h. After the solution had cooled it was evaporated at 0.6 mmHg and the muddy solid was treated with ether (70 cm^3) and stirred for 15 min. Upon settling, the ether was decanted and ether (250 cm^3) was again added to the solid which was neutralised with conc. HCl. The ether layer was again decanted and the solid was re-extracted with ether and conc. HCl. The combined ether layers were dried and evaporated to give 2,2-*dibromo*-3-*methylcyclopropane*-1,1-*dicarboxylic acid* **10b** (84%), m.p. 168–170 °C (Found: C, 24.2; H, 1.9. $C_6H_6Br_2O_4$ requires C, 23.9; H, 2.0%); $\delta_H(CD_3OD)$ 5.02 (2 H, br s), 2.51 (1 H, q, 6.5) and 1.32 (3 H, d, *J* 6.5); $\delta_C(CD_3OD)$ 168.7, 167.2, 47.4, 36.8, 33.3 and 14.4; ν_{max}(KBr)/cm^{-1} 3100br s (OH), 1701 s (C=O) and 1420s (C–H); *m/z* 142 (M − Br_2), 114 (M − $Br_2C_2H_4$) and 86 (M − $Br_2C_3H_4O$).

Hydrolysis of Diethyl 2,2-*Dibromo*-3-*pentylcyclopropane*-1,1-*dicarboxylate.*—Sodium metal (3.12 g, 0.135 mol) was dissolved in absolute ethanol (50 cm^3) as described above. When the solution had cooled, the dicarboxylate (7.0 g, 0.02 mol) and water (1.5 cm^3) were added to it and the mixture was refluxed for 1 h. Evaporation of the solvent at 0.6 mmHg afforded a muddy coloured solid which was treated with ether (70 cm^3) and stirred for *ca.* 15 min. Treatment as above gave 2,2-*dibromo*-3-*pentylcyclopropane*-1,1-*dicarboxylic acid* **10c** (80%), m.p. 146–148 °C (Found: C, 33.55; H, 3.95. $C_{10}H_{14}Br_2O_4$ requires C, 33.5; H, 3.95%); $\delta_H(CD_3OD)$ 5.2 (2 H, br s), 2.55 (1 H, br t), 1.7 (4 H, complex), 1.5 (4 H, complex) and 1.1 (3 H, br t); $\delta_C(CD_3OD)$ 168.2, 166.7, 46.9, 41.4, 32.9, 31.9, 30.0, 28.9, 23.85 and 14.6; ν_{max}/cm^{-1} 3000br s (OH), 1702s (C=O) and 1416s (CH_2).

Preparation of 1,1,2,2-*Tetrabromo*-3-*isopropylcyclopropane* **7a**.—*Method* (*a*). A solution of bromine (9.7 g, 60.6 mmol) in carbon tetrachloride (10 cm^3) was carefully added to a refluxing suspension of 2,2-dibromo-3-isopropylcyclopropane-1,1-dicarboxylic acid (10.0 g, 30.3 mmol) and red mercuric oxide 13.0 g, 60.6 mmol) in carbon tetrachloride (100 cm^3). After 3 h under reflux, the reaction mixture was allowed to cool and was then filtered. The filtrate was washed with 5% aqueous NaOH and then water. The organic layer was dried and evaporated to yield a clear yellow oil which solidified with time, and was identified as the *title compound* **7a** (which was purified by recrystallisation from methanol) (8.2 g, 68%), m.p. 47–49 °C (Found: C, 18.2; H, 1.8; M^+, 395.7362. $C_6H_8Br_4$ requires C, 18.01; H, 2.02%; *M*, 395.7356); δ_H 1.63 (1 H, d, *J* 2.4), 1.56 (1 H, m) and 1.17 (6 H, d, *J* 6.2); δ_C 51.0, 37.2, 31.3 and 17.8; ν_{max}/cm^{-1} 2961, 2928, 1738w, 1460m and 1387m; *m/z* 317/319/321/323 (M − Br), 238, 240, 242 (M − Br_2) and 159, 161 (M − Br_3).

Method (*b*). Bromine (1.95 g, 12 mmol) was added to a refluxing suspension of 2,2-dibromo-3-isopropylcyclopropane-1,1-dicarboxylic acid (2 g, 6.1 mmol) and red mercuric oxide (1.72 g, 7.9 mmol) in dichloromethane (10 cm^3). The suspension was refluxed for 3 h and then allowed to cool. The solids were filtered off and the filtrate was washed with aqueous sodium hydroxide (2 × 5 cm^3) and brine (2 × 5 cm^3), dried and evaporated to yield a yellow oil which solidified with time. After recrystallisation from methanol, the solid was identified as 1,1,2,2-*tetrabromo*-3-*isopropylcyclopropane* **7a** (0.87 g, 36%) (see spectral data above).

Method (*c*). Lead tetraacetate (5.41 g, 12.22 mmol) was added to a suspension of the title acid (2 g, 6.11 mmol) in carbon tetrachloride (10 cm^3) under a nitrogen atmosphere. The suspension was refluxed for 15 min before bromine (1.9 g, 12.22 mmol) was added to it. The reaction mixture was then illuminated with a tungsten lamp and refluxed until no further bromine was consumed. After the mixture had cooled, the precipitated solid was filtered off and the filtrate was washed with dilute perchloric acid (5 cm^3) and aqueous sodium hydrogen carbonate (5 cm^3), dried and evaporated to leave a pale yellow oil which solidified with time (1.8 g, 37%). The solid was recrystallised from methanol and identified as 1,1,2,2-*tetrabromo*-3-*isopropylcyclopropane*. All spectral data were identical with those described above. The aqueous layer was re-acidified to pH 1 and re-extracted with chloroform–methanol (10:1). The extract was dried and evaporated to afford a brown waxy solid (0.57 g). The NMR spectrum of this was extremely complicated but the mass spectrum confirmed the presence of starting material and 1,2,2-tribromo-3-isopropylcyclopropane-1-carboxylic acid (*m/z* 362, 317, 283 and 238).

1,1,2,2-*Tetrabromo*-3-*methylcyclopropane* **7b**.—Bromine (2.1 mol equiv.) in CCl_4 (7 cm^3) was added to a refluxing suspension of 2,2-dibromo-3-methylcyclopropane-1,1-dicarboxylic acid (2.5 g, 8 mmol) and red mercuric oxide (2.1 equiv.) in CCl_4 (20 cm^3). The mixture was refluxed for 3 h, after which no further bromine was consumed. After the mixture had cooled it was diluted with redistilled light petroleum (50 cm^3) and stirred

for 5 min. The suspension was then filtered through a sintered funnel containing flash silica. The filtrate was dried and evaporated to give the *title compound* **7b** (1.63 g, 53%) (Found: C, 13.3; H, 1.15. $C_4H_4Br_4$ requires C, 12.9; H, 1.08%); δ_H 2.1 (1 H, q, *J* 6.43) and 1.36 (3 H, d, *J* 6.43); δ_C 41.8, 40.9 and 15.9; *m/z* 289/291/293/295 (M − Br), 212/214/216 (M − Br_2) and 133/135 (M − Br_3).

1,1,2,2-*Tetrabromo*-3-*pentylcyclopropane* **7c**.—Bromine (2.1 mol equiv.) in CCl_4 (7 cm^3) was added to a refluxing suspension of 2,2-dibromo-3-pentylcyclopropane-1,1-dicarboxylic acid (1.5 g, 4 mmol) and red mercuric oxide (2.1 equiv.) in CCl_4 (20 cm^3). The mixture was refluxed for a further 3 h. After the mixture had cooled it was diluted with redistilled light petroleum (50 cm^3) and the mixture was stirred for 5 min. The suspension was then filtered through a sintered funnel containing flash silica. The filtrate was dried ($MgSO_4$) and evaporated at water pump pressure to afford the *title compound* **7c** as an oil (0.62 g, 35%) (Found: C, 22.9; H, 2.8. $C_8H_{12}Br_4$ requires C, 22.5; H, 3.0%); δ_H 1.9 (1 H, br t), 1.6 (4 H, br m), 1.3 (4 H, br m) and 0.9 (3 H, br t); δ_C 46.9, 40.0, 31.8, 31.3, 29.7, 26.7, 22.5 and 13.9.

Preparation of 1,2-*Dibromo*-3-*isopropylcyclopropene and Rearrangement to* 1,3-*Dibromo*-4-*methylpentyne*.—Methyllithium (1.5 mol dm^{-3}; 0.86 cm^3) was added to a solution of 1,1,2,2-tetrabromo-3-isopropylcyclopropane (0.44 g, 1.1 mmol) in dry ether (5 cm^3) at −78 °C. The reaction mixture was allowed to reach room temperature for 30 min before being cooled to −40 °C and quenched with water (1 cm^3). The ether was decanted from the ice, which was washed with further ether (2 × 2 cm^3). The combined organic fractions were dried and evaporated under reduced pressure to yield 1,2-*dibromo*-3-*isopropylcyclopropene* (180 mg, 70%); δ_H 2.49 (1 H, d, *J* 4.2), 1.85 (1 H, dq, *J* 4.2, 6.8) and 0.89 (6 H, d, *J* 6.8). The cyclopropene was found to be unstable and rearranged when stored for 16 h at 20 °C in deuteriochloroform to 1,3-*dibromo*-4-*methylpentyne*; this was purified by distillation (0.2 mmHg/15 °C) (130 mg, 72% conversion after distillation) (Found: M^+, 236.8916. $C_6H_7Br_2$ requires *M*, 236.8912); δ_H 4.46 (1 H, d, *J* 4.6), 2.05 (1 H, complex m), 1.11 (3 H, d, *J* 6.6) and 1.09 (3 H, d, *J* 6.6); δ_C 77.33s 48.11s, 45.46d, 35.76d, 19.66q and 19.22q; ν_{max}(film)/cm^{-1} 2967, 2932, 2208 and 1466.

Preparation of 3-*Bromo*-3-(1-*bromo*-3-*methylbut*-1-*enyl*)-1,1,2,2-*tetramethylcyclopropane* **13a**.—Methyllithium (1.5 mol dm^{-3}; 0.91 cm^3, 1.1 equiv.) was added over 1 min to a stirred solution of compound **7a** (0.5 g, 1.25 mmol) in dry ether at −78 °C. After the mixture had been allowed to reach room temperature, it was left for 40 min before being quenched with water (1 cm^3) at −40 °C. The mixture was shaken to obtain a clear solution after which the flask was cooled and the ether layer decanted from the remaining ice. The ice was washed with ether and the procedure repeated. 2,3-Dimethylbut-2-ene (1.05 g, 10 equiv.) was added to the combined ether layers after which the mixture was set aside at room temperature for 40 min and then evaporated to give a yellow oily solid exhibiting one peak by GLC. Distillation at 0.2 mmHg and 40 °C gave the *title compound* **13a** (0.28 g, 68%) (Found: M^+, 321.9933. $C_{12}H_{20}Br_2$ requires *M*, 321.9947); δ_H($CDCl_3$, 263 K) 5.69 (1 H, d, *J* 8.9), 2.65 (1 H, dq, *J* 8.9, 6.7), 1.33 (3 H, s), 1.21 (3 H, s), 1.18 (3 H, s), 1.11 (3 H, s) and 0.98 (6 H, d, *J* 6.7); δ_C 142.2d, 126.8s, 61.3s, 31.4d, 29.8s and 21.36q; ν_{max}/cm^{-1} 2963, 2931, 2871 and 1630; *m/z* 322/324/326, 307/309/311, 279/281/283 and 243/245.

Reaction of 1,1,2,2-*Tetrachloro*-3-*methylcyclopropane with Methyllithium*.—Methyllithium (1.89 cm^3, 2.8 mmol) was carefully added to a solution of 1,1,2,2-tetrachloro-3-methylcyclopropane (0.5 g, 2.6 mmol) and 2,3-dimethylbut-2-ene (2.1 cm^3, 28 mmol) in dry ether under a nitrogen atmosphere at −80 °C. The reaction mixture was left to reach room temperature and then stirred for a further 18 h before being cooled to −40 °C and quenched with water (1 cm^3). The ether layer was decanted from the ice which was washed with ether and the procedure repeated. The combined organic layers were dried and evaporated to leave a clear liquid which was distilled at 37 °C/0.6 mmHg and identified as 1-*chloro*-1-(1-*chloropropenyl*)-2,2,3,3-*tetramethylcyclopropane* (120 mg, 22%); δ_H 5.79 (1 H, q, *J* 6.6), 1.77 (3 H, d, *J* 6.6), 1.22 (6 H, s) and 1.17 (6 H, s); δ_C 135.98, 128.4, 66.38, 32.9, 29.5, 20.91, 20.35 and 15.1; *m/z* 206/208/210 and 191/193.

Preparation of Methyl 2-*Bromo*-2-(1-*bromo*-3-*methylbut*-1-*enyl*)-1-*methylcyclopropanecarboxylate* **16a**.—Methyllithium (1.5 mol dm^{-3}; 1.8 cm^3) was added to a solution of compound **7a** (1.0 g, 2.5 mmol) in dry ether at −80 °C. The mixture was then allowed to reach 0 °C at which temperature it was kept for 40 min before being cooled to −40 °C and quenched with water (1 cm^3). The ether layer was decanted from the ice and the ice washed with ether (2 × 2 cm^3); methyl methacrylate (2.5 cm^3, 10 equiv.) was then added to the combined ether fractions. The mixture was stirred at room temperature for 2 h and then dried and evaporated to give the *title compound* **16a** (600 mg, 70%) (which was purified by distillation at 60 °C/0.3 mmHg) (Found: M^+, 337.9518. $C_{11}H_{16}Br_2O_2$ requires *M*, 337.9512); δ_H 5.88 (1 H, d, *J* 8.9), 3.66 (3 H, s), 2.62 (1 H, m), 2.33 (1 H, d, *J* 6.5), 1.62 (3 H, s), 1.44 (1 H, d, *J* 6.5) and 0.99 (6 H, d, *J* 6.7); δ_C 170.88, 141.73, 125.57, 53.25, 50.4, 33.8, 31.29, 30.37, 21.8 and 21.38; *m/z* 338/340/342, 295/297/299 and 259/261; ν_{max}/cm^{-1} 2962s, 2869m, 1732s and 1457.

Hydrolysis of Methyl 2-*Bromo*-2-(1-*bromo*-3-*methylbut*-1-*enyl*)-1-*methylcyclopropanecarboxylate* **16a**.—(*a*) Trimethylsilyl iodide (0.4 cm^3, 3 mmol, 2 mol equiv.) was added to **16a** (0.5 g, 1.47 mmol) at room temperature after which the solution was heated to 80 °C and stirred for 75 min in the absence of light. The reaction mixture was then diluted with ether (5 cm^3) and washed with 5% aqueous NaOH (2 × 1 cm^3). The aqueous layer was then reacidified with 10% HCl and extracted with ether (3 × 2 cm^3), and the combined organic extracts were washed with aq. sodium thiosulfate, dried and evaporated to yield the 2-*bromo*-2-(1-*bromo*-3-*methylbut*-1-*enyl*)-1-*methylcyclopropanecarboxylic acid* **17a** (0.33 g, 70%) (Found: C, 37.1; H, 4.38. $C_{10}H_{14}Br_2O_2$ requires C, 37.05; H, 4.3%); δ_H 5.90 (1 H, d, *J* 9.0), 2.6 (1 H, m), 2.35 (1 H, d, *J* 6.6), 1.63 (3 H, s), 1.49 (1 H, d, *J* 6.6), 0.94 (3 H, d, *J* 6.7) and 0.96 (3 H, d, *J* 6.7); δ_C 176.9 (s), 141.8 (d), 124.9 (q), 50.9 (s), 33.7 (s), 31.8 (t), 31.5 (d), 21.7 (q) and 20.9 (q).

Work-up of the initial organic layer gave a second organic product; the above experiment was repeated several times in order to optimise its yield. The conditions for its preparation and its identity are described below.

(*b*) Trimethylsilyl iodide (1.2 g, 5.92 mmol) was added to the title ester (1 g, 2.96 mmol) at room temperature. The mixture was then heated to 60 °C and stirred in the absence of light whilst the reaction was monitored continuously by TLC. This showed that two products were forming at the same rate. After 90 min at 60 °C, no further starting material remained and the mixture was allowed to cool. The product was extracted with ether (3 × 5 cm^3), and the combined organic layers were washed with water, dried and evaporated to leave a pale yellow oil which was purified by column chromatography eluting with light petroleum and ether. The oil was provisionally identified as 4-*methylpent*-1-*ynyl* 2-*iodo*-1-*methylpropenoate* **18** (252 mg, 29%) (Found: M^+, 291.9962. $C_{10}H_{13}IO_2$ requires *M*, 291.9957); δ_H($CDCl_3$) 7.27 (1 H, s), 2.49 (2 H, d, *J* 6.7), 2.05 (1 H, m), 1.97

(3 H, s) and 0.93 (6 H, d, *J* 6.7); δ_C($CDCl_3$) 151.86, 132.7, 131.72, 90.3, 47.19, 30.38, 29.36, 22.4 and 11.62; *m/z* 292, 277, 249 and 167; ν_{max}(film)/cm^{-1} 3095, 2954, 1750 and 1613.

Rearrangement of 1,2-*Dibromo*-3-*isopropylcyclopropene in the Presence of* 2-*Methylpropene*.—Methyllithium (0.46 cm^3, 0.69 mmol) was added to a solution of compound **7a** (0.25 g, 0.63 mmol) in dry ether (5 cm^3) at −80 °C. The solution was allowed to reach room temperature and then stirred for a further 45 min before being cooled to −40 °C and quenched with water (1 cm^3). The ether layer was decanted from the ice and the ice washed with ether (2 × 2 cm^3). The combined organic layers were cooled to −50 °C and condensed 2-methylpropene (5 cm^3) was added to them. The solution was allowed to warm to room temperature over 2 h after which time a further quantity of 2-methylpropene (0.5 cm^3) was added to it. After 20 h the mixture was evaporated to leave a colourless oil which was distilled *in vacuo* (30 °C/0.4 mmHg) and identified as 1-*bromo*-1-(1-*bromo*-3-*methylbut*-1-*enyl*)-2,2-*dimethylcyclopropane* **22a** (110 mg, 59%) (Found: M^+, 295.9640. $C_{10}H_{16}Br_2$ requires *M*, 295.9612); δ_H 5.7 (1 H, d, *J* 8.8), 2.62 (1 H, m), 1.33 (3 H, s), 1.08 (3 H, s) and 0.92 (6 H, br t) (cyclopropane protons not clearly distinguishable); ν_{max}/cm^{-1} 2961, 2928, 2870 and 1466; *m/z* 296/298/300, 253/255/257 and 217/219.

Reaction of 1,2-*Dibromo*-3-*isopropylcyclopropene with Other Alkenes*.—Methyllithium (1.5 mol dm^{-3}; 1.05 mol equiv.) was added to a solution of compound **7a** (0.3 g, 0.7 mmol) in dry ether (5 cm^3) at −70 °C and the mixture stirred for *ca.* 5 min. The cooling bath was then removed and the temperature of the mixture was allowed to reach 0 °C. After quenching of the mixture with water (2 cm^3), the ether layer was decanted from the ice and the ice was washed with ether (2 × 5 cm^3). The ether fractions were combined and the alkene (10 equiv.) was added to them. The solution was stirred at room temperature for at least 3 h, after which the crude product was dried ($MgSO_4$) and evaporated.

(*a*) Methyl acrylate gave *methyl* 2-*bromo*-2-(1-*bromo*-3-*methylbut*-1-*enyl*)*cyclopropanecarboxylate* **24a**, purified by column chromatography eluting with light petroleum–ether (5:1) (33%) (Found: M^+, 323.9368. $C_{10}H_{14}Br_2O_2$ requires *M*, 323.9356); δ_H 5.9 (1 H, d, *J* 8.9), 3.7 (3 H, s), 2.6 (1 H, sept), 2.46 (1 H, dd, *J* 6.8, 8.9), 2.04 (1 H, t, *J* 6.5), 1.88 (1 H, dd, *J* 6.4, 8.9) and 0.99 (6 H, d, *J* 6.7); δ_C 168.5, 142.2, 123.0, 52.3, 40.7, 32.7, 31.0, 25.7, 21.2 and 21.0; ν_{max}/cm^{-1} 2961s (CH), 2869w (CH), 1738s (C=O), 1646w (C=C) and 1437s (CH_2); *m/z* 324/326/328 (M), 281/283/285 (M − C_3H_7) and 123 (M − $C_3H_7Br_2$).

(*b*) *cis*-But-2-ene gave a mixture of isomers of 3-*bromo*-3-(2-*bromo*-3-*methylbut*-1-*enyl*)-cis-1,2-*dimethylcyclopropane* **20a** and **21a** purified by column chromatography eluting with light petroleum–ether (10:1) (42%). GLC of the product showed two peaks very close together (For mixture, found: M^+, 293.9619. $C_{10}H_{16}Br_2$ requires *M*, 293.9614); δ_H 5.76 (1 H, overlapping d), 2.66 (1 H, sept), 1.73 (2 H, br q) and 1.2–0.96 (12 H, overlapping d); δ_C 144.1, 138.5, 131.3, 124.0, 54.7, 43.6, 31.4, 30.7, 29.7, 28.4, 24.7, 21.3, 21.2, 11.4 and 9.8; ν_{max}/cm^{-1} 2906s (CH), 2927w (CH), 1642w (C=C), 1465s (CH_2) and 660w (CBr); *m/z* 296/298/300 (M), 215/217 (M − Br), 135 (M − HBr_2) and 91 (M − $C_3H_7Br_2$).

(*c*) *trans*-But-2-ene gave 3-*bromo*-3-(2-*bromo*-3-*methylbut*-1-*enyl*)-trans-1,2-*dimethylcyclopropane* **19a** which was purified by column chromatography eluting with light petroleum–ether (10:1) (45%) and showed one peak on GLC (Found: M^+, 293.9619. $C_{10}H_{16}Br_2$ requires *M*, 293.9614); δ_H 5.76 (1 H, d, *J* 8.8), 2.66 (1 H, d sept, *J* 8.8, 6.6) and 1.75–0.96 [14 H, complex, including 1.36 (3 H, d, *J* 6.2), 1.1 (3 H, d, *J* 6.6) and 0.96 (6 H, overlapping d, *J* 6.6)]; δ_C 141.1, 32.4, 31.9, 29.7, 28.2, 22.7, 21.5, 21.3, 17.5 and 14.4; ν_{max}/cm^{-1} 2980s (CH), 2924s (CH), 2850w (CH) and 1465s (CH_2); *m/z* 294/296/298 (M), 136 (M − Br_2), 121 (M − CH_3Br_2) and 106 (M − $C_2H_6Br_2$).

Preparation of Methyl 2-*Bromo*-2-(1-*bromoprop*-1-*enyl*)-1-*methylcyclopropanecarboxylate* **16b**.—(*a*) Methyllithium (1.5 mol dm^{-3}; 1.05 mol equiv., 0.94 cm^3) was added to a solution of compound **7b** (0.5 g, 1.3 mmol) in dry ether (5 cm^3) at −70 °C and the mixture stirred for *ca.* 5 min. After this, the temperature was allowed to reach 0 °C. After the mixture had been quenched with water (2 cm^3) at −50 °C, the ether layer was decanted from the ice, and the ice was washed with ether (2 × 5 cm^3). Methyl methacrylate (1.35 g, 10 equiv.) was added to the ethereal extracts and the solution was stirred at room temperature for at least 3 h and then dried and evaporated to give the title compound **16b** (0.4 g, 95%). This was purified by column chromatography eluting with a mixture of light petroleum–ether (5:1) (Found: M^+, 311.9207. $C_9H_{12}Br_2O_2$ requires *M*, 311.9206) (0.17 g, 41%); δ_H 6.16 (1 H, q, *J* 6.5), 3.64 (3 H, s), 2.32 (1 H, d, *J* 6.45), 1.70 (3 H, d, *J* 6.5), 1.59 (3 H, s) and 1.44 (1 H, d, *J* 6.45); δ_C 170.21, 129.65, 128.0, 52.5, 49.9, 30.7, 20.5 and 16.95; ν_{max}/cm^{-1} 2945s (CH), 1729s (C=O) and 1447s (CH); *m/z* 310/312/314 (M), 231/233 (M − Br), 151 (M − Br_2) and 93 (M − $Br_2C_2H_3O_2$).

The above procedure was repeated using the following alkenes to trap the derived vinyl carbene:

(*b*) Methyl acrylate gave *methyl* 2-*bromo*-2-(1-*bromoprop*-1-*enyl*)*cyclopropanecarboxylate* **24b**, purified by column chromatography eluting with a mixture of light petroleum–ether (5:1) (42.5%) (Found: M^+, 297.9204. $C_8H_{10}{}^{79}Br^{81}BrO_2$ requires *M*, 297.9024); δ_H 6.22 (1 H, q, *J* 6.63), 3.70 (3 H, s), 2.44 (1 H, dd, *J* 6.8, 8.9), 2.04 (1 H, t, *J* 6.6) and 1.90 (1 H, dd, *J* 6.3, 8.90) and 1.75 (3 H, d, *J* 6.65); δ_C 170.1, 128.1, 125.32, 52.4, 49.7, 30.63, 20.42 and 16.84; ν_{max}/cm^{-1} 2951w (CH), 1737s (C=O), 1438 (CH_2), 1649 (C=CH) and 646 (CBr); *m/z* 296/298/300 (M), 217/219 (M − Br), 138 (M − Br_2), 95 (M − Br_2CO_2) and 70 (M − $Br_2C_2H_3O_2$).

(*c*) 2-Methylpropene gave 2-*bromo*-2-(1-*bromoprop*-1-*enyl*)-1,1-*dimethylcyclopropane* **22b** (Found: M^+; 267.9285. $C_8H_{12}{}^{79}Br^{81}Br$ requires *M*, 267.9282), purified by column chromatography eluting with a mixture of petroleum–ether (10:1) (55%); δ_H 6.05 (1 H, q, *J* 6.6), 1.74 (3 H, d, *J* 6.6), 1.39 (3 H, s), 1.3 (1 H, d, *J* 6.2), 1.21 (1 H, d, *J* 6.16) and 1.14 (3 H, s); δ_C 131.4, 127.93, 50.67, 30.33, 29.59, 25.35, 21.08 and 16.8; ν_{max}/cm^{-1} 2955s (CH), 2923s (CH), 1648s (C=C) and 1445s (CH_2); *m/z* 266/268/270 (M), 187/189 (M − HBr), 107 (M − HBr_2) and 93 (M − Br_2CH_2).

(*d*) *trans*-But-2-ene gave 3-*bromo*-3-(1-*bromoprop*-1-*enyl*)-trans-1,2-*dimethylcyclopropane* **19b**, purified by column chromatography eluting with a mixture of light petroleum–ether (10:1) (52%). GLC gave only one peak (Found: M^+, 267.9285. $C_8H_{12}{}^{79}Br^{81}Br$ requires *M*, 267.9282); δ_H 6.04 (1 H, q, *J* 6.6), 1.76 (3 H, d, *J* 6.6), 1.36 (3 H, d, *J* 6.2), 1.20 (1 H, p, *J* 6.6), 1.08 (3 H, d, *J* 6.05) and 0.86 (1 H, p, *J* 6.3); δ_C 130.65, 129.31, 50.60, 32.38, 28.1, 17.46, 17.02 and 14.36; ν_{max}/cm^{-1} 2960w (CH), 2927w (CH), 1649w (C=C), 1449s (CH_2) and 693 (CBr); *m/z* 266/268/270 (M), 187 (M − HBr), 107 (M − HBr_2) and 93 (M − Br_2CH_3).

(*e*) *cis*-But-2-ene gave two isomeric 3-*bromo*-3-(1-*bromoprop*-1-*enyl*)-cis-1,2-*dimethylcyclopropanes* **20b** and **21b**, purified by column chromatography eluting with light petroleum–ether (10:1) (56%). GLC showed two peaks very close together in ratio *ca.* 8:5, both different from the product obtained with *trans*-but-2-ene (For mixture, found: M^+, 267.9285. $C_8H_{12}{}^{79}Br^{81}Br$ requires *M*, 269.9282); δ_H 1.22 (2 H, complex), 1.06–1.2 (6 H, complex) for both isomers, plus 1.73 (3 H, d, *J* 6.9) and 6.08 (1 H, q, *J* 6.9) for the major isomer and

1.76 (3 H, d, *J* 6.9) and 6.1 (1 H, q, *J* 6.9) for the minor isomer; δ_C 134.36, 132.05, 127.04, 126.78, 54.44, 28.32, 24.45, 17.31, 16.63, 11.21 and 9.62; ν_{max}/cm^{-1} 2927s (CH), 1649w (C=C), 1447s (CH_2) and 676 (CBr); *m/z* 266/268/270 (M), 186/188 (M − HBr), 107 (M − HBr_2) and 92 (M − Br_2CH_4).

(*f*) The product from cyclohexene **23b**, which was a mixture of two isomers in ratio *ca.* 7:5, was purified by column chromatography eluting with light petroleum–ether (10:1) (38%); δ_H(two isomers) 6.07 (1 H, q, *J* 6.6), 1.71 (3 H, d, *J* 6.6); 6.24 (1 H, q, *J* 6.6) and 1.77 (3 H, d, *J* 6.6), together with complex signals at 1.0–2.3; δ_C 134.75, 132.05, 128.24, 126.59, 56.06, 43.25, 29.68, 28.10, 23.79, 20.91, 20.64, 20.59, 20.13, 17.47 and 16.79; ν_{max}/cm^{-1} 2934w (CH), 2856w (CH), 1649w (C=C), 1445w (CH_2) and 677w (CBr); *m/z* 292/294/296 (M), 212/214 (M − HBr), 133 (M − HBr_2) and 51 (M − $HBr_2C_6H_{10}$).

(*g*) 2,3-Dimethylbut-2-ene gave 3-*bromo*-3-(1-*bromoprop*-1-*enyl*)-1,1,2,2-*tetramethylcyclopropane* **13b** (60%) (Found: C, 40.6; H, 5.4. $C_{10}H_{16}Br_2$ requires C, 40.18; H, 5.37%); δ_H(−40 °C) 6.3 (1 H, q, *J* 6.6), 1.78 (3 H, d, *J* 6.6), 1.34 (3 H, s), 1.21 (3 H, s), 1.19 (3 H, s) and 1.10 (3 H, s); δ_H(25 °C) 6.03 (1 H, q, *J* 6.6), 1.77 (3 H, d, *J* 6.6), 1.30 (6 H, br s) and 1.47 (6 H, br s); δ_C(−40 °C) 130.55, 129.8, 61.5, 30.5, 28.4, 23.5, 21.6, 20.7, 18.9 and 17.5; ν_{max}/cm^{-1} 2922, 1645 and 1449.

Reaction of 1,2-*Dibromo*-3-*pentylcyclopropene with Alkenes.*—Methyllithium (1.5 mol dm^{-3}; 1.05 mol equiv.) was added to a solution of compound **7c** (0.3 g, 0.7 mmol) in dry ether (5 cm^3) at −70 °C. The mixture was stirred for *ca.* 5 min at that temperature and then allowed to reach 0 °C; after this it was cooled to −50 °C and quenched with water (2 cm^3). The ether layer was decanted and the ice was washed with ether (2 × 5 cm^3). The alkene (10 mol equiv.) was added to the combined ether fractions and the mixture was stirred at room temperature for at least 3 h. After this the crude product was dried and evaporated.

(*a*) 2-Methylpropene gave 2-*bromo*-2-(1-*bromohept*-1-*enyl*)-1,1-*dimethylcyclopropane* **22c**, purified by column chromatography using light petroleum–ether (5:1) as eluent (44%) (Found: M^+, 323.9906. $C_{12}H_{20}{}^{79}Br^{81}Br$ requires *M*, 323.9911); δ_H 5.96 (1 H, t, *J* 7.0), 2.10 (2 H, q, *J* 7.0), 1.54 (2 H, br s), 1.35 (3 H, complex m), 1.33–1.23 (6 H, complex m), 1.11 (3 H, complex m) and 0.84 (3 H, complex m); δ_C 133.4, 130.2, 50.8, 40.0, 31.3, 31.1, 27.7, 25.5, 21.2 and 13.9; ν_{max}/cm^{-1} 2955s (CH), 1642w (C=C), 1457s (CH_2) and 667w (CBr); *m/z* 322/324/326 (M), 243/245 (M − Br) and 251/253/255 (M − C_5H_{11}).

(*b*) *cis*-But-2-ene gave the two isomeric 3-*bromo*-3-(1-*bromohept*-1-*enyl*)-cis-1,2-*dimethylcyclopropanes* **20c** and **21c** purified by column chromatography using light petroleum–ether (5:1) as eluent (66%). GLC showed two peaks in ratio of *ca.* 1:2 (For mixture, found: M^+, 323.9906. $C_{12}H_{20}{}^{79}Br^{81}Br$ requires *M*, 323.9911); δ_H 5.97 (1 H, overlapping t), 2.13 (2 H, overlapping q), 0.9–1.6 (14 H, complex) and 0.8 (3 H, br t); δ_C 137.6, 133.2, 132.2, 125.8, 54.6, 43.6, 30.96, 29.5, 28.3, 27.7, 27.5, 24.5, 11.2 and 9.7; ν_{max}/cm^{-1} 2956s (CH), 2856w (CH), 1642w (C=C), 1458s (CH_2) and 671w (CBr); *m/z* 322/324/326 (M).

(*c*) *trans*-But-2-ene gave 3-*bromo*-3-(1-*bromohept*-1-*enyl*)-trans-1,2-*dimethylcyclopropane* **19c** (Found: M^+, 323.9906. $C_{12}H_{20}{}^{79}Br^{81}Br$ requires *M*, 323.9906), purified by column chromatography using light petroleum–ether (5:1) as eluent (44%). GLC showed only one peak, different from the two isomers obtained from *cis*-but-2-ene; δ_H 5.97 (1 H, t, *J* 7.0), 2.18 (2 H, q, *J* 7.0), 1.37 (3 H, d, *J* 6.2), 1.1 (3 H, d, *J* 6.0), 1.26 (8 H, complex m) and 0.9 (3 H, complex m); δ_C 14.5, 17.5, 22.4, 28.2, 29.4, 29.7, 31.4, 32.0, 32.4, 50.8, 129.5 and 134.8; ν_{max}/cm^{-1} 2957s (CH), 2856s (CH), 1644w (C=C), 1453s (CH_2) and 688w (CBr); *m/z* 322/324/326 (M).

(*d*) Methyl acrylate gave *methyl* 2-*bromo*-2-(1-*bromohept*-1-*enyl*)*cyclopropanecarboxylate* **24c** (Found: M^+, 351.9675. $C_{12}H_{20}Br_2O_2$ requires *M*, 351.9668), purified by column chromatography eluting with light petroleum–ether (5:1) (44%); δ_H 6.2 (1 H, t, *J* 7.0), 3.7 (3 H, s) [minor second Me signal at 3.8 (< 10%)], 2.42 (1 H, dd, *J* 6.8, 8.9), 2.18 (2 H, q, *J* 7), 2.07 (1 H, t, *J* 6.6), 1.92 (1 H, dd, *J* 6.4, 8.9), 1.24 (6 H, br m) and 0.84 (3 H, t, *J* 6.3); δ_C 168.6, 136.3, 125.2, 52.4, 40.8, 32.6, 31.3, 27.5, 22.5 and 14.0; ν_{max}/cm^{-1} 3400br (OH), 2954w (CH), 1737s (C=O), 1646w (C=C) and 1438 (CH_2); *m/z* 352/354/356 (M).

(*e*) 2,3-Dimethylbut-2-ene gave 3-*bromo*-3-(1-*bromohept*-1-*enyl*)-1,1,2,2-*tetramethylcyclopropane* **13c** (54%) (Found: M^+, 350.0238. $C_{14}H_{24}Br_2$ requires *M*, 350.0249); δ_H 5.8 (1 H, t, *J* 7), 2.16 (2 H, q, *J* 7), 1.26 (12 H, v br), 1.12 (6 H, s) and 0.87–0.81 (3 H, t, *J* 6.6); δ_C 136.0, 129.2, 61.5, 31.7, 31.4, 29.7, 27.7, 22.5 and 14.0; *m/z* 271/273 (M − Br).

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