A Regio- and Stereo-selective Route to 1,1,3- and 1,2,3-Trihalogenobutadienes by Dehydrohalogenation of Alkyl-substituted 1,1,2,3-Tetrahalogenocyclopropanes

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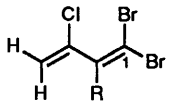
Non-terminal alkenes vicinally substituted with chlorine are converted into 2,3-dialkyl-1,1,2,3-tetrahalogenocyclopropanes on reaction with dichlorocarbene generated under phase-transfer conditions, or dibromocarbene generated either by phase transfer or from the thermolysis of phenyl(tribromomethyl)mercury. 1,1,2,3-Tetrahalogenocyclopropanes are also obtained by reaction of the corresponding vicinal bromochloro- and dibromo-alkenes with dichlorocarbene under phase-transfer conditions or of the latter alkenes with phenyl(tribromomethyl)mercury. The tetrahalides produced undergo ring-opening when heated in the presence of quinoline, overall elimination of hydrogen halide leading to specifically substituted trihalogenobutadienes.

Dihalogenocyclopropanes have been shown to undergo a range of transformations of synthetic value.[1] More recently, the chemistry of 1,1,2-trihalogeno- and 1,1,2,2-tetrahalogeno-cyclopropanes has been examined, and their thermal ring opening to halogenated dienes,[2] silver-induced ring opening,[3] and 1,2-dehalogenation to synthetically versatile 1-halogeno- or 1,2-dihalogenocyclopropenes,[4] have been reported. The cyclopropanes are readily available by addition of dihalogenocarbenes to the corresponding 1-halogeno- or 1,1-dihalogenoalkene, although these are generally much less reactive towards the carbenes than are the corresponding non-halogenated alkenes.[5] As part of a route to halogenated natural products we required a simple approach to 2-alkylbutadienes substituted at positions 1 and 3 with two different halogens, *e.g.* compound (**1**). These could reasonably be derived by deprotonation of the allyl ion (**2**), in turn derived from cyclopropane (**3**) by selective loss of bromide ion from C-2. In order to obtain such cyclopropanes we have examined the addition of dihalogenocarbenes to 1,2-dihalogenoalkenes. The addition of bromochlorocarbene and dichlorocarbene, generated by the Seyferth route, to (*E*)- and (*Z*)-1,2-dichloroethenes has been reported to lead to cyclopropanes,[6] whereas the corresponding addition of dibromocarbene leads in addition to a rearranged tetrahalogenopropene.[7] When the carbene is generated from non-metallic sources, no reaction occurs with (*E*)-1,2-dichloroethene.[7] Dichlorocarbene generated under phase-transfer conditions does, however, add to the more reactive 1,2-dichloro-1,2-diethoxyethene.[8] Tetrahalogenocyclopropanes have also been obtained by addition of halogens to 3,3-dihalogenocyclopropenes,[9] and by an ene-reaction between alkenes and tetrachlorocyclopropene.[10]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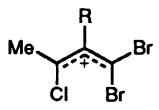
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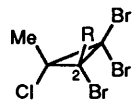
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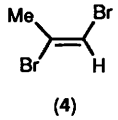
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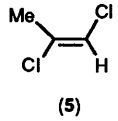
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The alkenes (**4**) and (**5**) were recovered unchanged when they were stirred rapidly with chloroform, catalytic cetrimide* and aqueous 25M sodium hydroxide at 20 °C for 5 days. However, under the same conditions the dihalogenoalkenes (**6**), (**7**)[11] and (**8**)[12] (R = H, Me, Et) were converted into the corresponding 1,1,2,3-tetrahalogenocyclopropanes (**9**)–(**11**) in yields ranging from 53–67% (Table 1); the iodochloride (**12**) was not cyclopropanated under these conditions. The ^{13}C NMR spectra of the cyclopropanes were consistent with the formation of a single stereoisomer in each case, assigned as the *E*-form. The signals for C-1 occurred at *ca.* δ 71, a position typical of other geminal dichlorocyclopropanes,[1b] while C-2 and C-3 were observed at 49–59, and were 5–10 ppm further downfield for bromine substituents than for chlorine when other substituents were identical. The dichlorides (**8**) could also be dibromocyclopropanated under phase-transfer conditions to give (**13**; R = H, Me, Et).

Compounds (**13**; R = H, Me) were also obtained on refluxing the dichloroalkenes (**8**; R = H, Me) with phenyl(tribromomethyl)mercury in benzene for 3 days. There was no evidence of formation of any ring-opened products in these reactions similar to those observed in the corresponding reactions of (*E*)- or (*Z*)-1,2-dichloroethene.[7] The ^{13}C NMR spectra were again consistent with the formation of a single stereoisomer of the cyclopropane, and the carbon bearing the geminal bromines

Table 1. Dihalogenocyclopropanation of alkenes.

Alkene	R	Cyclopropane	Conditions	Yield (%)
(**6**)	H	(**9**)	$CHCl_3$, base	55
(**6**)	Me	(**9**)	$CHCl_3$, base	53
(**6**)	Et	(**9**)	$CHCl_3$, base	67
(**8**)	H	(**11**)	$CHCl_3$, base	57
(**8**)	Et	(**11**)	$CHCl_3$, base	61
(**8**)	H	(**13**)	$PhHgCBr_3$	77
(**8**)	Me	(**13**)	$PhHgCBr_3$	75
(**6**)	H	(**15**)	$PhHgCBr_3$	69
(**7**)	H	(**10**)	$CHCl_3$, base	57
(**7**)	Me	(**10**)	$CHCl_3$, base	55
(**7**)	Et	(**10**)	$CHCl_3$, base	53
(**8**)	Me	(**11**)	$CHCl_3$, base	55
(**8**)	H	(**13**)	$CHBr_3$, base	42
(**8**)	Me	(**13**)	$CHBr_3$, base	71
(**8**)	Et	(**13**)	$CHBr_3$, base	53
(**6**)	Me	(**15**)	$PhHgCBr_3$	67

* Cetyltrimethylammonium bromide, $CH_3(CH_2)_{15}N(CH_3)_3Br$.

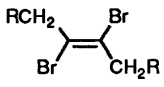
Table 2. Relative reactivities of alkenes towards dihalogenocyclopropanation.

Alkenes		Conditions	Product ratio
(16; X = Cl)	(8, R = H)	$CHCl_3$ (PTC)	5:1
(16; X = Cl)	(8; R = H)	$PhHgCBr_3$	5:1
(16; X = Cl)	(8, R = H)	$CHBr_3$ (PTC)	12:1
(16; X = Br)	(6, R = H)	$CHCl_3$ (PTC)	11.4:1

Table 3. Thermolysis of tetrahalogenocyclopropanes.

Cyclopropane	*t*/min	*T*/°C	Product	Yield (%)
(9; R = H)	30	160	(17; R = H)	65
(9; R = Me)	75	180	(17; R = Me) (18; R = Me)	63
(9; R = Et)	60	200	(17; R = Et) (18; R = Et)	67
(10; R = H)	45	160	(20; R = H)	64
(10; R = Me)	60	180	(20; R = Me)	61
(10; R = Et)	90	200	(20; R = Et)	67
(13; R = H)	30	180	(22; R = H)	61
(13; R = Me)	30	180	(22; R = Me)	63
(13; R = Et)	45	200	(22; R = Et)	65
(11; R = H)	90	200	(20; R = H) (24; R = H)	51
(11; R = Me)	120	200	(20; R = Me) (24; R = Me)	55
(11; R = Et)	160	200	(20; R = Et) (24; R = Et)	57

appeared at δ 46–48, again typical for such compounds.[1b] The stereochemistry was confirmed as *E*- by reduction of (13; R = Me) to (14), which showed seven signals in the ^{13}C spectrum as expected for the isomer with the alkyl groups *E*-related.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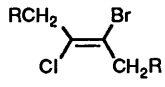
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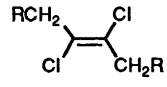
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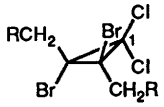
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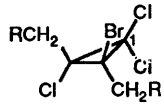
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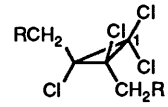
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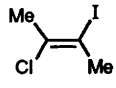
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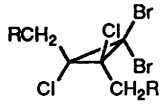
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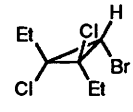
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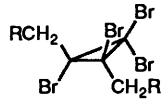
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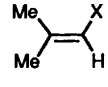

(16)

Treatment of the dibromoalkenes (6; R = H, Me, Et) or the bromochloroalkenes (7; R = H, Me, Et) with bromoform under identical phase-transfer conditions failed to afford any tetrahalogenocyclopropanes and starting material was recovered. However, the tetrabromocyclopropanes (15; R = H, Me) were obtained on treatment of dibromoalkenes (6; R = H, Me), respectively, with phenyl(tribromomethyl)mercury in benzene at reflux for 3 days.

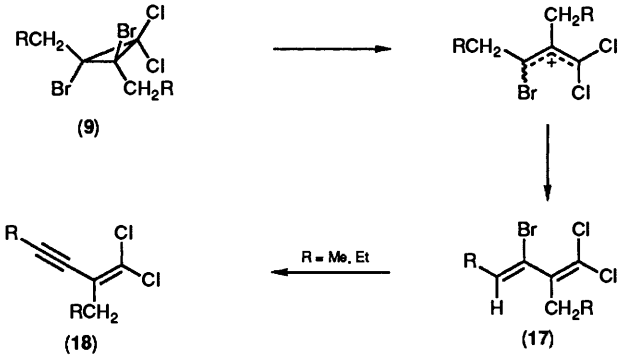
In order to assess the relative reactivity of 1,2-dihalogenoalkenes towards dihalogenocarbenes, competition studies were carried out between (8; R = H) and 1-chloro-2-methylprop-1-ene (16; X = Cl) and between (6; R = H) and 1-bromo-2-methylprop-1-ene (16; X = Br), either with bromoform or chloroform under phase-transfer conditions or phenyl(tribromomethyl)mercury in refluxing benzene. One mol. equiv. of each of the dihalogeno- and monohalogeno-alkanes was allowed to react with a deficiency of the dihalogenocarbene, and the ratios of the products were determined by GLC, correcting for the relative responses of the two products. The results (Table 2) indicate that the monohalogenoalkenes are somewhat more reactive towards dihalogenocarbenes than are the 1,2-dihalogenoalkenes.

When the 1,1,2,3-tetrahalogenocyclopropanes (9)–(11) and (13) were subjected to thermolysis in quinoline at temperatures ranging from 160–200 °C for 30–160 min, the corresponding trihalogeno dienes were furnished in moderate yields (Table 3). When more than one isomer was produced, they were separated by preparative GLC for characterisation.

The results may be summarised as follows:

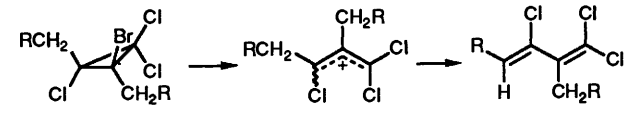
(i) Where a choice existed, the tetrahalides reacted by loss of hydrogen bromide rather than hydrogen chloride. Although the mechanism of thermolysis has not been absolutely established, it may involve the loss of a halide anion and concerted ring opening to a halogenoallyl cation, followed by deprotonation in the presence of quinoline.[13]

(ii) The dibromo dichloride (9; R = H) reacted by loss of bromide ion, leading to halide (17; R = H); in the same way compound (10; R = H) was converted into compound (20; R = H):



(9) (17) (18)

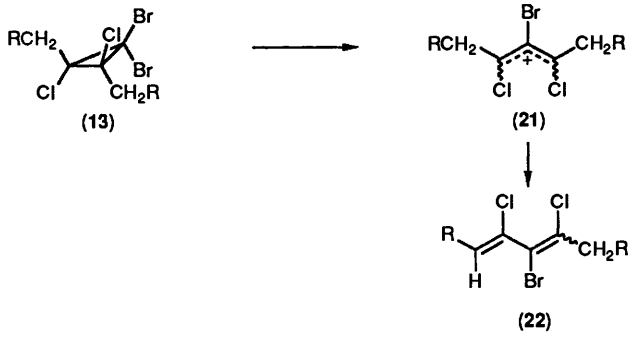
(iii) The bromo trichlorides (10; R = Me, Et) each gave a single isomer of the corresponding diene (20; Me, Et), characterised as *Z*- on steric grounds.


(10) (19) (20)

Although 3-bromo-1,1-dichlorobutadiene,[14] 1,1,3-tribromobutadiene,[15] and 1,1,3-trichlorobutadiene,[16] have been widely reported, reports of their homologues are very limited, *e.g.*, (*E*)- and (*Z*)-1,1,3-trichloropenta-1,3-diene,[17] and 1,1-dibromo-3-chlorohepta-1,3-diene.[18]

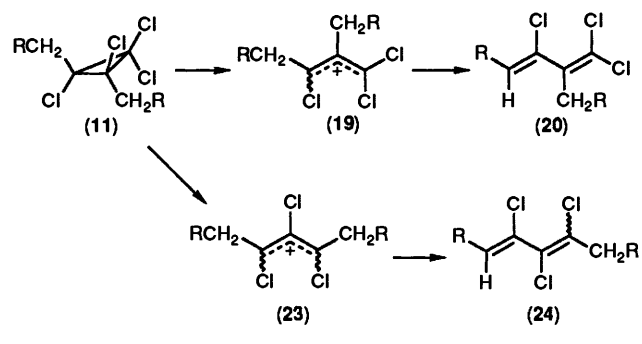
(iv) Thermolysis of compound (9; R = Me, Et) led initially to a single isomer of the corresponding diene (17; R = Me, Et); by analogy with (iii) this is the *Z*- form. However, before all the starting material had been consumed the diene began to react further to produce the alkyne (18; R = Me, Et); indeed at longer reaction times, this was the exclusive product.

(v) Loss of the geminal halogen was the exclusive process for compound (**13**; R = H), leading to a 1:1 mixture of *E*- and *Z*-isomers of compound (**22**; R = H). Although the configuration of these could not be decided with certainty, the compound with the higher field methyl signal is probably *E*-, placing this in the shielding zone of the vinyl group.

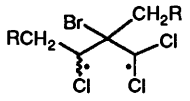


(vi) The halides (**13**; R = Me, Et) also reacted by loss of bromide ion, preference for this overcoming that for the loss of the halogen geminal to the alkyl substituent. Again a mixture of two stereoisomers of the diene was obtained in each case. Since halide (**13**; R = H) also led to two isomers, it is assumed that the two products are isomeric about the tetrasubstituted rather than the trisubstituted double bond.

(vii) The major product from compound (**11**; R = H) was identical to compound (**20**; R = H), indicating that the chlorine geminal to the methyl group was lost in preference to one of the geminal dichlorides. However, two minor isomeric products (*ca.* 10 and 3%, respectively of the major product) were also observed. Each showed two doublets in the alkene region of the ^{1}H NMR spectrum (*J ca.* 1.7 Hz) and a methyl singlet. They are assigned to the two isomers of compound (**24**; R = H), derived by loss of one of the geminal chlorines. The tetrachlorides (**11**; R = Me, Et) also gave the corresponding diene (**20**), again as a single stereoisomer; this did not react further under the reaction conditions. Two additional products were isolated in each case, corresponding to the isomeric dienes (**24**), one of which was the major reaction product in each case. Although there are a number of reports of 1,2,3-substituted trichloro-,[19] tribromo-,[20] dibromochloro-,[21] and bromodichlorobutadienes,[22] their homologues are not widely reported.



Although the mechanism of thermolysis of the above cyclopropanes has been represented as the loss of a halide anion and ring opening to a halogenoallyl cation, followed by deprotonation in the presence of quinoline,[13] a diradical process *via, e.g.*, species (**25**) is also plausible.[23] Whatever the mechanism, the above reactions do allow ready access to single stereoisomers of 1,1-dichloro-3-bromoalka-1,3-dienes and to *E*/*Z*-mixtures of 1,2,3-trihalogenoalkadienes; the stereochemistry of the products could, in principle, be controlled by a concerted disrotatory opening and loss of halide ion, but it is likely that isomerisation would occur under the reaction conditions.



(25)

Experimental

Unless otherwise stated, all new compounds were homogeneous by TLC and/or GLC; NMR spectra were run in $CDCl_3$ solution and recorded for ^{1}H at 200 or 300 MHz on Bruker instruments, and ^{13}C spectra were recorded at the corresponding carbon frequency on the same instruments. IR spectra were obtained on a Nicolet 20SX, while mass spectra were measured on an AEI MS9 or a Kratos MS80 instrument using the EI method; where mass measurements are quoted for chlorine-containing species, they refer to ^{35}Cl isotope peaks. M.p.s are uncorrected. All experiments involving methyl-lithium were carried out under dry nitrogen. Light petroleum refers to the fraction boiling between 40–60 °C. Organic layers were dried with $MgSO_4$ before removal of the solvent. Column chromatography was carried out over silica. Vicinal dihalogenoalkenes were prepared as previously described.[11,12]

Addition of Dichlorocarbene to 1,2-*Dihalogenoalkenes under Phase-transfer Catalysis.*—An aqueous solution of NaOH (6 ml; 25M) was added dropwise to a mixture of dibromoalkene (4.72 mmol) and cetrimide (0.1 g, 0.28 mmol) in $CHCl_3$ (13 ml) over 10 min with vigorous stirring. The mixture was stirred efficiently over 5 days and then poured into brine (50 ml). Extraction into CH_2Cl_2 (2 × 25 ml), followed by washing with brine (2 × 50 ml), drying ($MgSO_4$) and concentration under reduced pressure gave the crude product. Addition of ether (50 ml) and filtration of any insoluble material, followed by concentration of the filtrate under reduced pressure afforded the corresponding dibromodichlorocyclopropanes.

2,3-Dibromobut-2-ene gave 2,3-*dibromo*-1,1-*dichloro*-2,3-*dimethylcyclopropane* (**9**; R = H) (0.76 g, 55%), m.p. 83–85 °C (recrystallised from MeCN) (Found: C, 20.4; H, 2.0. $C_5H_6Br_2Cl_2$ requires C, 20.23; H, 2.04%); δ_H 2.1 (6 H, s); δ_C 28.7 (q), 49.4 (s), and 70.6 (s); ν_{max} 2 934m, 2 855m, 1 440s, 1 377s, 1 217m, 1 046s, 883s, and 708 s cm^{-1}.

3,4-Dibromohex-3-ene gave 2,3-*dibromo*-1,1-*dichloro*-2,3-*diethylcyclopropane* (**9**; R = Me) (0.74 g, 53%), m.p. 121–123 °C (recrystallised from MeOH) (Found: C, 25.8; H, 3.0. $C_7H_{10}Br_2Cl_2$ requires C, 25.88; H, 3.10%); δ_H 1.2 (6 H, t, *J* 7 Hz), and 2.2 (4 H, q, *J* 7 Hz); ν_{max} 2 978s, 2 878m, 1 456s, 1 379m, 1 201m, 1 092m, 838s, and 787m cm^{-1}.

4,5-Dibromo-oct-4-ene gave 2,3-*dibromo*-1,1-*dichloro*-2,3-*dipropylcyclopropane* (**9**; R = Et) which was purified by flash chromatography with light petroleum and ether (10:1) as eluant (0.93 g, 67%) (Found: C, 30.4; H, 4.0. $C_9H_{14}Br_2Cl_2$ requires C, 30.63; H, 4.00%); δ_H 0.99 (6 H, t, *J* 7 Hz), 1.67 (4 H, sextet, *J* 7 Hz), and 1.97–2.24 (4 H, complex mult); δ_C 13.6 (q), 21.1 (t), 42.3 (t), 55.5 (s), and 71.0 (s); ν_{max} 2 917s, 2 849s, 1 471m, 1 378m, 1 221m, 1 090m, 912m, and 778m cm^{-1}.

2,3-Dichlorobut-2-ene gave 1,1,2,3-*tetrachloro*-2,3-*dimethylcyclopropane* (**11**; R = H) (0.55 g, 57%), m.p. 68–70 °C (recrystallised from EtOH) (Found C, 28.8; H, 2.80. $C_5H_6Cl_4$ requires C, 28.88; H, 2.91%); ν_{max} 2 938m, 2 880m, 1 444s, 1 379m, 1 216m, 1 056s, 898s, and 759s cm^{-1}; δ_H 1.9 (6 H, s); δ_C 23.2 (q), 55.3 (s), and 70.1 (s).

3,4-Dichlorohex-3-ene gave 1,1,2,3-*tetrachloro*-2,3-*diethylcyclopropane* (**11**; R = Me) which was purified by flash column chromatography as above (0.61 g, 55%) (Found: C, 35.5; H, 4.05. $C_7H_{10}Cl_4$ requires C, 35.63; H, 4.27%); δ_H 1.1 (6 H, t, *J* 7 Hz),

and 2.1 (4 H, q, *J* 7 Hz); ν_{max} 2 938m, 2 881m, 1 459s, 1 380m, 1 201m, 1 016m, 858s, and 731m cm^{-1}.

4,5-Dichloro-oct-4-ene gave 1,1,2,3-*tetrachloro*-2,3-*dipropylcyclopropane* (**11**; R = Et) which was purified by flash chromatography as above (0.75 g, 61%) (Found C, 40.8; H, 5.2. $C_9H_{14}Cl_4$ requires C, 40.94; H, 5.34%); δ_H 0.98 (6 H, t, *J* 7 Hz), 1.56–1.75 (4 H, complex multiplet), and 2.05 (4 H, multiplet); δ_C 13.7 (q), 19.5 (t), 37.8 (t), 59.8 (s), and 71.1 (s); ν_{max} 2 965m, 2 874m, 1 470s, 1 380m, 1 260m, 1 015m, 878m, and 759s cm^{-1};

2-Bromo-3-chlorobut-2-ene gave 3-*bromo*-1,1,2-*trichloro*-2,3-*dimethylcyclopropane* (**10**; R = H) (0.67 g, 57%), m.p. 79–81 °C (recrystallised from EtOH) (Found: C, 23.6; H, 2.3. $C_5H_6BrCl_3$ requires C, 23.80; H, 2.40%); δ_H 1.8 (3 H, s), and 1.9 (3 H, s); δ_C 20.2 (q), 23.2 (q), 46.3 (s), 55.3 (s), and 70.1 (s); ν_{max} 2 938m, 1 440s, 1 380m, 1 215m, 1 055s, 891s, and 760s cm^{-1}.

3-Bromo-4-chlorohex-3-ene gave 3-*bromo*-1,1,2-*trichloro*-2,3-*diethylcyclopropane* (**10**; R = Me) which was purified by flash chromatography as above (0.72 g, 55%) (Found: C, 29.8; H, 3.4. $C_7H_{10}BrCl_3$ requires C, 29.98; H, 3.59%); δ_H 1.23 (6 H, t, *J* 7 Hz), 2.15 (2 H, q, *J* 7 Hz), and 2.20 (2 H, q, *J* 7 Hz); ν_{max} 2 977m, 2 880m, 1 458s, 1 381m, 1 050m, 852m, and 787s cm^{-1}.

4-Bromo-5-chloro-oct-4-ene gave 3-*bromo*-1,1,2-*trichloro*-2,3-*dipropylcyclopropane* (**10**; R = Et) which was purified by flash chromatography as above (0.77 g, 53%) (Found: C, 34.9; H, 4.4. $C_9H_{14}BrCl_3$ requires C, 35.04; H, 4.57%); δ_H 0.98 (3 H, t, *J* 7 Hz), 0.99 (3 H, t, *J* 7 Hz), 1.55–1.75 (4 H, complex mult), and 1.97–2.23 (4 H, complex multiplet); ν_{max} 2 980s, 2 880m, 1 460m, 1 379m, 1 047m, 847m, and 785m cm^{-1}.

Reaction of Dichloroalkenes with Bromoform under Phase-transfer Catalysis.—An aqueous solution of NaOH (6 ml; 25M) was added dropwise to the dichloroalkene (8 mmol), bromoform (1.1 ml; 12 mmol) and cetrimide (0.1 g, 0.28 mmol) in CH_2Cl_2 (15 ml) over 10 min with vigorous stirring. The mixture was stirred efficiently for 5 days and then poured into brine (50 ml). Extraction into CH_2Cl_2 (2 × 25 ml) followed by washing with brine (2 × 50 ml), drying ($MgSO_4$) and concentration under reduced pressure gave the crude product. Addition of ether (50 ml) and filtration of any insoluble material with subsequent concentration under reduced pressure afforded the dibromodichlorocyclopropane.

2,3-Dichlorobut-2-ene gave 1,1-*dibromo*-2,3-*dichloro*-2,3-*dimethylcyclopropane* (**13**; R = H) (42%), m.p. 85–87 °C (recrystallised from EtOH) (Found C, 20.0; H, 1.9. $C_5H_6Br_2Cl_2$ requires C, 20.23; H, 2.04%); ν_{max} 2 982m, 2 932m, 1 440s, 1 375m, 1 215m, 1 050s, 820s, and 760s cm^{-1}; δ_H 1.99 (6 H, s); δ_C 22.9 (q), 55.4 (s), and 47.7 (s).

3,4-Dichlorohex-3-ene gave 1,1-*dibromo*-2,3-*dichloro*-2,3-*diethylcyclopropane* (**13**; R = Me) (71%), m.p. 123–125 °C (recrystallised from EtOH) (Found: C, 25.7; H, 2.9. $C_7H_{10}Br_2Cl_2$ requires C, 25.88; H, 3.10%); ν_{max} 2 975s, 2 879m, 1 458s, 1 379m, 1 100m, 880m, and 796s cm^{-1}; δ_H 1.21 (6 H, t, *J* 7 Hz), and 2.18 (4 H, q, *J* 7 Hz); δ_C 10.5 (q), 31.9 (t), 46.9 (s), and 60.7 (s).

4,5-Dichloro-oct-4-ene gave, after work up and flash chromatography as above, 1,1-*dibromo*-2,3-*dichloro*-2,3-*dipropylcyclopropane* (**13**; R = Et) (1.49 g, 53%) as a colourless oil (Found: C, 30.4; H, 3.9. $C_9H_{14}Br_2Cl_2$ requires C, 30.63; H, 4.00%); ν_{max} 2 964s, 2 874m, 1 461s, 1 380m, 1 110m, 806m, and 744 m cm^{-1}; δ_H 0.99 (6 H, t, *J* 7 Hz), 1.67 (4 H, sextet, *J* 7 Hz), and 1.85–2.20 (4 H, complex mult); δ_C 13.7 (q), 19.7 (t), 39.9 (t), 47.5 (s), and 59.8 (s).

Preparation of Tetrahalogenocyclopropanes using Phenyl(tribromomethyl)mercury.—The bromoalkene (2.36 mmol) was added to the phenyl(tribromomethyl)mercury (2.5 g, 4.72 mmol) in dry benzene (10 ml) and refluxed for 3 days. The mixture was filtered through silica gel (Merck 7736) using a sinter column and the column was washed with light petroleum (2 × 10 ml). The combined filtrates were concentrated under reduced pressure to afford the corresponding tetrabromocyclopropane.

2,3-Dibromobut-2-ene gave 1,1,2,3-*tetrabromo*-2,3-*dimethylcyclopropane* (**15**; R = H) (0.62 g, 69%), m.p. 125–127 °C (recrystallised from benzene and light petroleum) (Found: C, 15.4; H, 1.4. $C_5H_6Br_4$ requires C, 15.57; H, 1.57%); ν_{max} 2 929m, 2 852m, 1 439s, 1 376s, 1 212m, 1 047s, 766m, and 656s cm^{-1}; δ_H 2.1 (6 H, s).

3,4-Dibromohex-3-ene gave 1,1,2,3-*tetrabromo*-2,3-*diethylcyclopropane* (**15**; R = Me) (0.65 g, 67%), m.p. 163–165 °C (recrystallised from benzene and light petroleum) (Found: C, 20.2; H, 2.3. $C_7H_{10}Br_4$ requires C, 20.32; H, 2.44%); δ_H 0.9 (6 H, t, *J* 7 Hz), and 2.2 (4 H, q, *J* 7 Hz).

2,3-Dichlorobut-2-ene gave (**13**; R = H) (0.53 g, 77%) identical to that obtained above.

3,4-Dichlorohex-3-ene gave (**13**; R = Me) (0.570 g, 75%) identical to that obtained above.

Competition between 2,3-Dichlorobut-2-ene and 1-Chloro-2-methylprop-1-ene for Dichlorocarbene under Phase-transfer Catalysis.—An aqueous solution of NaOH (3 ml; 25M) was added dropwise to 2,3-dichlorobut-2-ene (0.50 g, 5.52 mmol), 1-chloro-2-methylprop-1-ene (0.70 g, 5.52 mmol), cetrimide (0.1 g, 0.28 mmol) and $CHCl_3$ (0.23 ml, 2.76 mmol) over 5 min with vigorous stirring. The mixture was monitored by GLC every 15 min until the peaks of the products remained constant. The average ratio obtained after correcting for the different GLC sensitivities of the two products was *ca.* 5:1 in favour of 1,1,3-trichloro-2,2-dimethylcyclopropane over compound (**11**; R = H).

Competition between 2,3-Dichlorobut-2-ene and 1-Chloro-2-methylprop-1-ene for Dibromocarbene under Phase-transfer Catalysis.—Aqueous NaOH (3 ml; 25M) was added dropwise to 2,3-dichlorobut-2-ene (0.50 g, 5.52 mmol), 1-chloro-2-methylprop-1-ene (0.70 g, 5.52 mmol), cetrimide (0.1 g, 0.28 mmol) and $CHBr_3$ (0.24 ml, 2.76 mmol) in CH_2Cl_2 (10 ml) over 5 min with vigorous stirring. The mixture was monitored by GLC every 15 min until the peaks of products remained constant. The average ratio obtained after correcting for the different GLC responses of the products was *ca.* 12:1 in favour of 1,1-dibromo-3-chloro-2,2-dimethylcyclopropane over (**13**; R = H).

Competition between 2,3-Dichlorobut-2-ene and 1-Chloro-2-methylprop-1-ene for Dibromocarbene using Phenyl(tribromomethyl)mercury.—Phenyl(tribromomethyl)mercury (1.46 g, 2.76 mmol) was refluxed with 2,3-dichlorobut-2-ene (0.50 g, 5.52 mmol) and 1-chloro-2-methylprop-1-ene (0.70 g, 5.52 mmol) in dry benzene (10 ml). The mixture was monitored by GLC every 15 min as above. The average ratio obtained after correcting for the different sensitivities of the two products towards GLC was *ca.* 5:1 in favour of 1,1-dibromo-3-chloro-2,2-dimethylcyclopropane over (**13**; R = H).

Competition between 2,3-Dibromobut-2-ene and 1-Bromo-2-methylprop-1-ene for Dichlorocarbene under Phase-transfer Catalysis.—Aqueous NaOH (3 ml; 25M) was added to 2,3-dibromobut-2-ene (0.48 g, 3.50 mmol), 1-bromo-2-methylprop-1-ene (0.74 g, 3.50 mmol), cetrimide (0.1 g, 0.28 mmol) and $CHCl_3$ (0.14 ml, 1.73 mmol) in CH_2Cl_2 (10 ml) over 5 min with vigorous stirring. The mixture was monitored by GLC every 15 min until the peaks of the products remained constant. The average ratio obtained was *ca.* 11.4:1 in favour of 3-bromo-1,1-dichloro-2,2-dimethylcyclopropane over (**9**; R = H).

3-*Bromo*-1,2-*dichloro*-1,2-*diethylcyclopropane.*—Sodium borohydride (2.0 g) was added over 1 h to a stirred solution of

the dibromide (**13**; R = Me) (2.0 g) in distilled methanol (30 ml) under nitrogen in an ice-bath. The reaction was monitored by GLC; when all the starting material had been consumed, the solvent was removed at 14 mmHg and the remaining oil was dissolved in ether (20 ml) and washed with water (2 × 20 ml), brine (20 ml) and dried. Work-up as before gave an oil (0.8 g); this showed two peaks in the ratio 9:1 on GLC. The major component was collected and characterised as (*E*)-3-bromo-1,2-dichloro-1,2-diethylcyclopropane[Found: 208.9804 (M^+ − Cl). Calc. for $C_7H_{11}BrCl$: 208.9732]; δ_H 3.33 (1 H, s), 2.05–1.95 (4 H, m), 1.18 (3 H, t, *J* 7 Hz), and 1.15 (3 H, t, *J* 7 Hz); δ_C 57.1, 55.4, 32.0, 29.3, 10.7, and 9.7. The minor component was shown by GC–MS to be of formula $C_7H_{12}Cl_2$.

Preparation of Trihalogenodienes from 1,1,2,3-*Tetrahalogenocyclopropanes by Thermolysis in Quinoline.*—The tetrahalogenocyclopropane (2 mmol) was added to the quinoline (7 ml) and heated at 160–200 °C for 1–2.5 h, as specified below. The mixture was then poured into dil. HCl (15 ml), extracted into ether (2 × 10 ml) and washed successively with saturated aq. $NaHCO_3$ (10 ml), water (10 ml) and brine (10 ml), dried ($MgSO_4$) and concentrated under reduced pressure to afford the corresponding trihalogeno dienes. When more than one isomer was produced, they were separated by preparative GLC.

Compound (**9**; R = H) gave 3-*bromo*-1,1-*dichloro*-2-*methylbuta*-1,3-*diene* (**17**; R = H) after 30 min at 160 °C (0.28 g, 65%) (Found: M^+, 213.9345. $C_5H_5BrCl_2$ requires *M*, 213.9356); ν_{max} 2 923m, 1 632m, 1 598m, 1 218m, 1 083m, 914s, and 787s cm^{-1}; δ_H 2.04 (3 H, s), 5.78 (1 H, d, *J* 2.1 Hz), and 5.75 (1 H, d, *J* 2.1 Hz); δ_C 20.4 (q), 120.5 (s), 121.6 (s), 126.9 (t), and 134.8 (s).

Compound (**9**; R = Me) gave 5,5-*dichloro*-4-*ethylpent*-4-*en*-2-*yne* (**18**; R = Me) and 3-*bromo*-1,1-*dichloro*-2-*ethylpenta*-1,3-*diene* (**17**; R = Me) (ratio *ca.* 1:1 by GLC), after 75 min at 180 °C (0.20 g, 63%). The *alkyne* (Found: M^+, 162.0018. $C_7H_8Cl_2$ requires *M*, 162.0003); ν_{max} 2 976m, 2 225w, 1 578m, 1 461m, 1 376m, 1 068w, 890m, and 786s cm^{-1}; δ_H 1.11 (3 H, t, *J* 7 Hz), 2.04 (3 H, s), and 2.32 (2 H, q, *J* 7 Hz); δ_C 13.6 (q), 36.5 (t), 40.5 (q), 77.2 (s), 100.2 (s), 121.6 (s), and 140.2 (s). The *diene* (Found: M^+, 241.9268. $C_7H_9BrCl_2$ requires *M*, 241.9265); ν_{max} 2 975m, 1 594m, 1 458m, 1 216m, 1 107m, 910m, and 786s cm^{-1}; δ_H 1.0 (3 H, t, 7 Hz), 1.8 (3 H, d, *J* 6 Hz), 2.4 (2 H, q, *J* 7 Hz), and 5.8 (1 H, q, *J* 6 Hz); δ_C 13.6 (q), 20.4 (t), 26.4 (q), 121.7 (s), 127.4 (d), and 140.8 (s), The above reaction was repeated and followed by GLC. At short reaction times two peaks were observed, corresponding to starting material and the diene (**17**; R = Me); after 1 h the starting material had disappeared and the peak for the alkyne was present. After 4 h at 180 °C, GLC showed that all the diene had been consumed and only the alkyne remained. Work-up as above gave the crude alkyne (76%) which was purified by flash distillation.

Compound (**9**; R = Et) gave 6,6-*dichloro*-5-*propylhex*-5-*en*-3-*yne* (**18**; R = Et) and 3-*bromo*-1,1-*dichloro*-2-*propylhexa*-1,3-*diene* (**17**; R = Et) (ratio *ca.* 1:1 by GLC) after 60 min at 200 °C (0.26 g, 67%). The *alkyne* (Found: M^+, 190.0318. $C_9H_{12}Cl_2$ requires *M*, 190.0316); ν_{max} 2 964s, 2 874m, 2 225w, 1 580m, 1 460m, 1 318m, 927s, and 880m cm^{-1}; δ_H 0.94 (3 H, t, *J* 7 Hz), 1.20 (3 H, t, *J* 7 Hz), 1.57 (2 H, sextet, *J* 7 Hz), and 2.20–2.44 (4 H, complex mult); δ_C 13.6 (q), 13.9 (q), 21.1 (t), 36.4 (t), 42.8 (t), 77.1 (s), 100.5 (s), 121.9 (s), and 140.3 (s). The *diene* (Found: M^+, 269.9580. $C_9H_{13}BrCl_2$ requires *M*, 269.9578); ν_{max} 2 964s, 2 873m, 1 696m, 1 460m, and 918m cm^{-1}; δ_H 0.93 (3 H, t, *J* 7 Hz), 1.05 (3 H, *J* 7 Hz), 1.47 (2 H, sextet, *J* 7 Hz), 2.24 (2 H, p, *J* 7 Hz), 2.35 (2 H, t, *J* 7 Hz), and 5.8 (1 H, t, *J* 7 Hz); δ_C 13.7 (q), 13.8 (q), 21.2 (t), 26.4 (t), 28.6 (t), 121.8 (s), 127.3 (d), and 140.2 (s).

Compound (**10**; R = H) gave 2-*methyl*-1,1,3-*trichlorobuta*-1,3-*diene* (**20**; R = H) after 45 min at 160 °C (0.22 g, 64%) (Found: M^+, 169.9305. $C_5H_5Cl_3$ requires *M*, 169.9307); ν_{max} 2 924w, 1 630m, 1 600s, 1 221s, 1 089m, 1 033m, 912s, and 670m cm^{-1}; δ_H 2.04 (3 H, s), 5.75 (1 H, d, *J* 2.1 Hz), and 5.78 (1 H, d, *J* 2.1 Hz); δ_C 19.9, 117.6, 121.0, 133.3, and 136.9.

Compound (**10**; R = Me) gave 2-*ethyl*-1,1,3-*trichloropenta*-1,3-*diene* after 60 min at 180 °C (0.24 g, 61%) (Found: M^+, 197.9766. $C_7H_9Cl_3$ requires *M*, 197.9770); ν_{max} 2 975m, 2 875m, 1 658w, 1 596m, 1 459m, 1 220m, 923s, and 878s cm^{-1}; δ_H 1.04 (3 H, t, *J* 7 Hz), 1.83 (3 H, d, *J* 7 Hz), 2.42 (2 H, q, *J* 7 Hz), and 5.74 (1 H, q, *J* 7 Hz); δ_C 11.4, 14.3, 26.6, 120.7, 127.0, 127.1, and 139.8.

Compound (**10**; R = Et) gave 2-*propyl*-1,1,3-*trichlorohexa*-1,3-*diene* (**20**; R = Et) after 90 min at 200 °C (0:30 g, 67%) (Found: M^+, 226.0081. $C_9H_{13}Cl_3$ requires *M*, 226.0083); ν_{max} 2 968s, 2 875m, 1 610w, 1 460m, 1 375m, 920m, and 780m cm^{-1}; δ_H 0.93 (3 H, t, *J* 7 Hz), 1.04 (3 H, t, *J* 7 Hz), 1.46 (2 H, sextet, *J* 7 Hz), 2.27 (2 H, p, *J* 7 Hz), 2.39 (2 H, t, *J* 7 Hz), 5.66 (1 H, t, *J* 7 Hz); δ_C 12.7 (q), 13.7 (q), 20.4 (t), 22.3 (t), 35.0 (t), 121.1 (s), 127.5 (d), 133.9 (s), and 138.5 (s).

Compound (**11**; R = H) gave three products in the ratio *ca.* 10:1:1 after 90 min at 200 °C (0.17 g, 51%). The major product was compound (**20**; R = H) identical to that obtained above. The minor products were characterised as the isomeric 2,3,4-trichloropenta-2,4-dienes (**24**; R = H), although their NMR data were too similar to allow a simple distinction to be made. The second isomer (M^+, 169.9473) showed δ_H 2.32 (3 H, s), 5.59 (1 H, d, *J* 1.7 Hz), and 5.67 (1 H, d, *J* 1.7 Hz). The third isomer (M^+, 169.9467) showed δ_H 2.31 (3 H, s), 5.50 (1 H, d, *J* 1.5 Hz), and 5.64 (1 H, d, *J* 1.5 Hz).

Compound (**11**; R = Me) gave three compounds in the ratio 1:2:0.75 by GLC, after 120 min at 200 °C (0.22 g, 55%). The first compound was identical to 2-ethyl-1,1,3-trichloropenta-1,3-diene obtained above. The second compound (M^+, 197.9794) showed ν_{max} 2 990m, 1 615m, 1 460m, 1 180w, 1 130, 940s, 785s, and 710 cm^{-1}; δ_H 1.17 (3 H, t, *J* 7.5 Hz), 1.86 (3 H, d, *J* 6.8 Hz), 2.63 (2 H, q, *J* 7.5 Hz), and 6.00 (1 H, q, *J* 6.8 Hz). The third isomer (M^+, 197.9795) showed ν_{max} 2 980m, 1 610m, 1 460m, 1 190w, 935s, 815s, 780, and 685 cm^{-1}; δ_H 1.16 (3 H, t, *J* 7.4 Hz), 1.86 (3 H, d, *J* 6.7 Hz), 2.53 (2 H, q, *J* 7.4 Hz), and 5.94 (1 H, q, *J* 6.7 Hz).

Compound (**11**; R = Et) gave a mixture of (**20**; R = Et) and (E)- and (Z)-2-*propyl*-1,1,3-*trichlorohexa*-1,3-*dienes* (**24**; R = Et) (ratio *ca.* 1:6:1 by GLC), after 160 min at 200 °C (0.26 g, 57%). The mixture (M^+, 226.0083. $C_9H_{13}Cl_3$ requires *M*, 226.0083) showed ν_{max} 2 967s, 2 875m, 1 609w, 1 460m, 1 380w, 917m, and 787m cm^{-1}; δ_H 0.97 (3 H, t, *J* 7 Hz), 1.06 (3 H, t, *J* 7 Hz), 1.66 (2 H, sextet, *J* 7 Hz), 2.29 (2 H, t, *J* 7 Hz), 2.59 (2 H, t, *J* 7 Hz), together with two triplets at 5.86 (1 H, t, *J* 7 Hz), and 5.91 (1 H, t, *J* 7 Hz) in ratio 1:6, and all the signals quoted above for (**20**; R = Et).

Compound (**13**; R = H) gave (E)- and (Z)-3-*bromo*-2,4-*dichloropenta*-1,3-*diene* (**22**; R = H) (ratio *ca.* 1:1 by GLC) after 30 min at 180 °C (0.26 g, 61%). The E-*isomer* (Found: M^+, 213.8955. $C_5H_5BrCl_2$ requires *M*, 213.8952); ν_{max} 2 920m, 1 630m, 1 590m, 1 214m, 1 079m, 914s, and 781s cm^{-1}; δ_H 2.35 (3 H, s), 5.56 (1 H, d, *J* 1.7 Hz), and 5.61 (1 H, d, *J* 1.7 Hz). The Z-*isomer* (Found: M^+, 213.8958. $C_5H_5BrCl_2$ requires *M*, 213.8952); ν_{max} 2 923m, 1 627m, 1 590m, 1 216m, 1 080m, 914s, and 780s cm^{-1}; δ_H 2.30 (3 H, s), 5.49 (1 H, d, *J* 1.5 Hz), and 5.59 (1 H, d, *J* 1.5 Hz).

Compound (**13**; R = Me) gave (Z,E)- and (Z,Z)-4-*bromo*-3,5-*dichlorohepta*-2,4-*diene* (**22**; R = Me) (ratio *ca.* 2.5:1 by GLC) in 30 min at 180 °C (63%). The *first isomer* (Found: M^+, 241.9297. $C_7H_9BrCl_2$ requires *M*, 241.9265) showed ν_{max} 2 980m, 1 615m, 1 460m, 1 380, 1 285, 1 175, 1 125m, 940s, 800, 795s, and 695 cm^{-1}; δ_H 1.17 (3 H, t, *J* 7.4 Hz), 1.84 (3 H, d, *J* 6.8 Hz), 2.66 (2 H, q, *J* 7.5 Hz), and 5.97 (1 H, q, *J* 6.7 Hz); δ_C 11.3, 14.6, 32.3, 114.4, 129.3, 129.6, and 136.5. The *second isomer* (Found: M^+, 241.9390); ν_{max} 2 980m, 1 600m, 1 460m, 1 380,

1 280m, 1 180, 1 120m, 930s, 805, 750s, and 680 cm^{-1}; δ_H 1.16 (3 H, t, *J* 7.4 Hz), 1.85 (3 H, d, *J* 6.7 Hz), 2.54 (2 H, q, *J* 7.4 Hz), and 5.93 (1 H, q, *J* 6.7 Hz); δ_C 12.9, 14.7, 30.6, 117.6, 128.6, 130.0, and 142.4.

Compound (**13**; R = Et) gave (Z,E)- and (Z,Z)-5-*bromo*-4,6-*dichloronona*-3,5-*dienes* (**22**; R = Et) (ratio *ca.* 1:1 as determined by GLC) after 45 min at 200 °C. (0.35 g, 65%). The *first isomer* (Found: M^+, 269.9574. $C_9H_{13}BrCl_2$ requires *M*, 269.9578); ν_{max} 2 967s, 2 874m, 1 606m, 1 460m, 1 164w, 909m, and 739s cm^{-1}; δ_H 1.02 (3 H, t, *J* 7 Hz), 1.06 (3 H, t, *J* 7 Hz), 1.67 (2 H, sextet, *J* 7 Hz), 2.26 (2 H, p, *J* 7 Hz), 2.63 (2 H, t, *J* 7 Hz), and 5.98 (1 H, t, *J* 7 Hz). The *second isomer* (Found: M^+, 269.9568. $C_9H_{13}BrCl_2$ requires *M*, 269.9578); ν_{max} 2 967s, 2 874m, 1 601m, 1 460m, 1 170w, 908m, and 736s cm^{-1}; δ_H 0.92 (3 H, t, *J* 7 Hz), 1.05 (3 H, t, *J* 7 Hz), 1.65 (2 H, sextet, *J* 7 Hz), 2.27 (2 H, p, *J* 7 Hz), 2.51 (2 H, t, *J* 7 Hz), and 5.84 (1 H, t, *J* 7 Hz); δ_C 12.5, 13.3, 21.3, 22.5, 38.7, 118.1, 128.6, 141.0, and 135.5.

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