

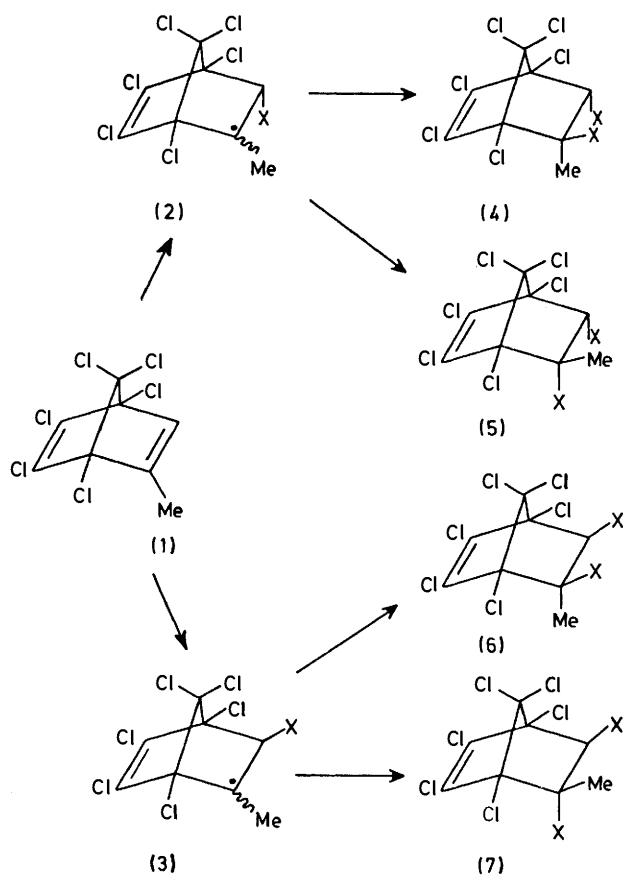
## Free Radical Reactions of Halogenated Bridged Polycyclic Compounds Part 18.<sup>1</sup> The Addition of Chlorine and Bromine to 1,2,3,4,7,7-Hexachloro-5-methylnorbornadiene

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The addition of chlorine and bromine to 1,2,3,4,7,7-hexachloro-5-methylnorbornadiene affords the respective 1 : 1 adducts of the addition of the elements of chlorine and bromine to the 5,6-double bond. In each case the two *cis* and the two *trans* isomers are formed. Such compounds are also formed when the elements of chlorine are provided from oxalyl chloride. Product formation is discussed in terms of the various factors involved in the radical-addition and chain-transfer steps of the reaction.

As a continuation of the studies in this series concerning the factors which control free-radical addition to chlorine-substituted norbornadienes,<sup>2</sup> an investigation of the addition of chlorine and bromine to 5-methylhexachloronorbornadiene (1) has been carried out. The addition of chlorine to the diene (1) in carbon tetrachloride solution afforded the 1 : 1 addition products (4A), (5A), (6A), and (7A) derived from the four possible modes of addition of chlorine to the 5,6-double bond (Scheme 1). Product proportions are reported in Table 1.

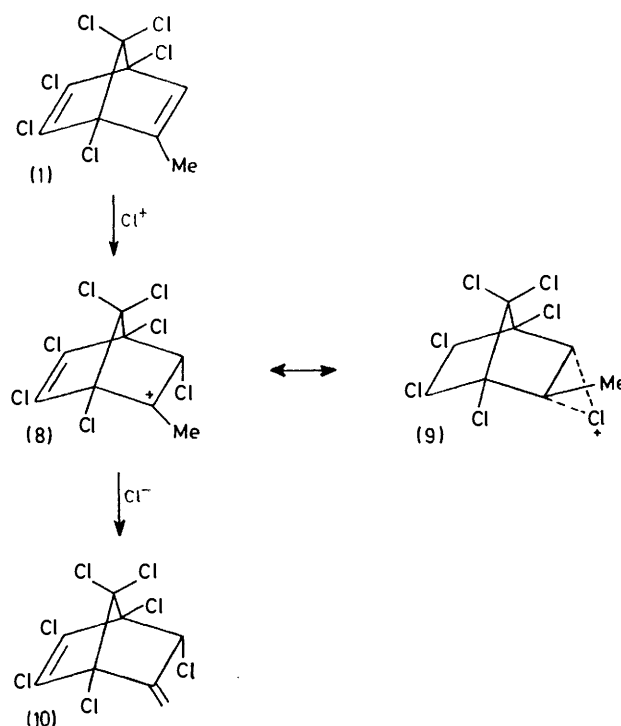
The reaction conditions were chosen in order to achieve



A; X = Cl; B; X = Br; C; X = SR

SCHEME 1

the free-radical addition of the elements of chlorine, and it is proposed that the free-radical pathway outlined in Scheme 1 is followed. Support for this proposal was provided by the formation of the same products, and in



SCHEME 2

the same proportions, when oxalyl chloride, a known<sup>3</sup> free-radical reagent, is the source of chlorine. In addition to the 1 : 1 adducts listed in Table 1, both reactions of (1) with chlorine and with oxalyl chloride

TABLE 1

Ratio of products formed in the addition of chlorine and bromine to diene (1)

Halogen source	Solvent	Product distribution (%)				X
		(4)	(5)	(6)	(7)	
Cl <sub>2</sub>	CCl <sub>4</sub>	17	23	40	20	Cl
(COCl) <sub>2</sub>	None	17	23	40	20	Cl
Br <sub>2</sub>	CCl <sub>4</sub>	15	14	12	59	Br
Br <sub>2</sub>	AcOH-H <sub>2</sub> SO <sub>4</sub>	27	23	7	47	Br

afforded polychlorinated products to the extent of *ca.* 10% of the reaction product. Individual polychlorinated compounds could not be isolated from the reaction mixture, but mass spectral analysis suggested that compounds of molecular formulae  $C_8HCl_{13}$ ,  $C_8H_2Cl_{12}$ ,  $C_8HCl_{11}$ , and  $C_8Cl_{12}$  were present.

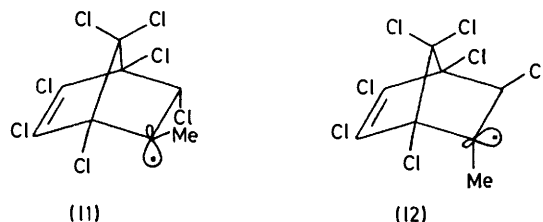
In an attempt to accomplish the addition of chlorine to diene (1) by an ionic pathway, (1) was treated with chlorine in acetic acid as solvent, to which concentrated sulphuric acid had been added. No addition products were formed and 1,2,3,4,6-*endo*-7,7-hexachloro-5-methylenenorborn-2-ene (10) was the sole product (Scheme 2). Compound (10) was identified by the similarity of its n.m.r. spectrum with that of the corresponding 6-*endo*-bromo-derivative.<sup>4</sup> The formation of (10) may be envisaged as taking place *via* a carbonium ion (8) or a chloronium ion intermediate (9) resulting from attack by the electrophile  $Cl^+$  on diene (1). The absence of products (4A)—(7A) in this reaction, and the absence of (10) from the reaction of diene (1) with chlorine in carbon tetrachloride, is further evidence for the free-radical nature of the reaction of diene (1) with chlorine in carbon tetrachloride.

Products (4A)—(7A) are the sole 1:1 addition products that result from the proposed free-radical addition of chlorine to diene (1). No products of rearrangement are formed as is the case in the free-radical addition of thiols to the diene (1).<sup>2</sup> This is unlikely to be due to steric factors in the chain-transfer step since it is improbable that it is easier for a chlorine molecule to approach intermediates (2A) and (3A) than it is for the relatively small hydrogen-end of a thiol molecule to approach the intermediate (3C) from thiyl radical addition. Therefore the more efficient chain-transfer of (2A) and (3A) with chlorine, than of (3C) with thiol, may be best rationalised on the basis of the weaker bond strength of the Cl—Cl bond ( $239 \text{ kJ mol}^{-1}$ )<sup>5</sup> compared to the S—H bond in a thiol (*e.g.* MeS—H,  $293 \text{ kJ mol}^{-1}$ ).<sup>5</sup> However the free-radical addition of the elements of chlorine to hexachloronorbornadiene<sup>6</sup> results in the formation of products of rearrangement and indicates that in the intermediates (2) and (3) the radical centre is stabilised by the methyl substituent to some extent.

Both *endo* and *exo* attack of a chlorine atom on diene (1) occurs to give intermediates (2A) and (3A), whereas only *endo* attack leading to (2C) is apparently involved in the attack of thiyl radicals on diene (1).<sup>2</sup> Since the covalent radius of a chlorine atom is 99 pm compared to 104 pm for sulphur this observation is unlikely to be explicable on steric grounds, and is probably a reflection of the respective differences of the electrostatic attraction of thiyl radicals and chlorine atoms for the diene (1). Previous work<sup>7</sup> on free-radical additions to chlorine-substituted norbornenes and norbornadienes has led to the conclusion that the greater the electrophilic character possessed by a free radical the greater is its tendency for *exo* attack. In this case, in spite of the steric factors making *exo* attack relatively unfavourable, it can nevertheless occur since the chlorine

atom may be considered to have some electrophilic character.

The preferential formation of the *cis-exo* isomer (6A) relative to the *trans* isomer (7A), and of the *cis-endo* isomer (5A) relative to the *trans* isomer (4A), indicates that in the intermediate radicals (2A) and (3A) the substituents at C-5 and C-6 have a preference for assuming a *trans* arrangement as in (11) and (12), in which steric interaction between proximate methyl and chlorine substituents is minimised. Additionally such



intermediates allow for any bridging or interactions between the chlorine substituent and the radical centre. The small preference for the formation of (5A) over (4A) than that of (6A) over (7A) is a result of the unfavourable torsional strain<sup>8</sup> in the *endo* chain-transfer step leading to the formation of (5A).

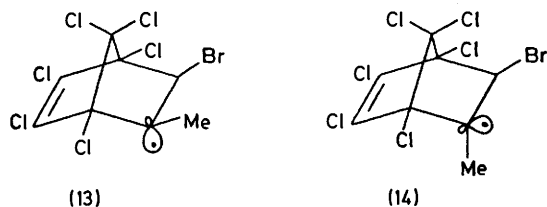
The addition of bromine to the diene (1) in carbon tetrachloride solution is comparable to the addition of chlorine and affords the 1:1 addition products (4B)—(7B) in the proportions given in Table 1. In an attempt to achieve an ionic pathway the reaction was also performed in acetic acid as solvent, to which quinol and sulphuric acid had been added, to respectively inhibit free radical and promote ionic reaction. Products (4B)—(7B) were again formed, but as shown in Table 1 they were in a somewhat different ratio. The amounts of (4B) and (5B) were increased relative to (6B) and (7B), which could suggest that (4B) and (5B), at least under these conditions, have a partial origin in an ionic addition of bromine. The major difference between the addition of chlorine in carbon tetrachloride solution to diene (1) compared with the addition of bromine is that the ratio of (6) to (7) changes from 2:1 to 1:5. This suggests that for chain-transfer with the larger bromine molecule, product development control is important for the conversion of (3B) to (6B) and (7B). Due to the respective atomic sizes of bromine and chlorine the eclipsing of the methyl group in (7B) by bromine is more unfavourable than the eclipsing of the methyl group in (6B) by chlorine. However the torsional strain preference<sup>8</sup> for *exo* chain-transfer of (3B) with bromine leading to (6B) than of *endo* chain-transfer of (3B) leading to (7B) outweighs the fact that structure (13) is likely to be favoured less than (14). The structures of (4)—(7) were based on their respective n.m.r. spectral data. Table 2 shows that for each compound both the hydrogen at C-6 and the methyl group at C-5 appear as singlets. In accordance with previous observations a methyl group attached to a carbon bearing a halogen group occurs at higher field when in the *exo*-position

TABLE 2

N.m.r. spectral data (60 MHz) for the products of the addition of chlorine and bromine to the diene (1)

Compound	X	Me		H	
		Position	$\delta$ (s)	Position	$\delta$ (s)
(4A)	Cl	5-endo	2.14	6-exo	4.74
(4B)	Br	5-endo	2.43	6-exo	4.94
(5A)	Cl	5-exo	1.69	6-exo	5.18
(5B)	Br	5-exo	1.90	6-exo	5.22
(6A)	Cl	5-endo	2.18	6-endo	4.70
(6B)	Br	5-endo	2.31	6-endo	4.62
(7A)	Cl	5-exo	1.63	6-endo	4.54
(7B)	Br	5-exo	1.68	6-endo	4.62

than when *endo*;<sup>9</sup> in contrast an *endo* hydrogen is found at higher field than an *exo* hydrogen.<sup>10</sup> Further support for these structures was provided by the observation that compound (7A) was comparatively stable to base,



(5A) reacted partially, whereas (4A) and (6A) readily lost hydrogen chloride. This is in accordance with previous observations on the dehydrohalogenation of norbornenes, where the ease of loss of hydrogen chloride is *exo-cis* > *trans* > *endo-cis*.<sup>11</sup> The more ready loss of *trans* disposed atoms of hydrogen and chlorine from (6A) than from (5A) is probably due to the less sterically crowded, and hence more approachable, 6-*endo* hydrogen in (6A) compared with the 6-*exo* hydrogen in (5A).

The results make it clear that product formation in free radical addition reactions to chlorine-substituted norbornadienes is dependent on the relative importance of the following factors: (i) steric and electrostatic interactions between the attacking radical and the diene; (ii) steric and electrostatic interactions between functional groups in the intermediate radicals; (iii) steric and electrostatic interactions between the chain-transfer molecule and the intermediate radical; and (iv) torsional strain factors in both the radical attack on the double bond and in the chain-transfer step.

#### EXPERIMENTAL

N.m.r. spectra were recorded at 60 MHz using a Perkin-Elmer R12B instrument. G.l.c. analyses were performed on a Perkin-Elmer F-11 gas chromatograph (using nitrogen as carrier gas at a pressure of  $20.7 \times 10^4$  Pa) fitted with a 2-m  $\times$   $\frac{1}{8}$ -in stainless-steel column packed with 5% Apiezon L on AW-DMCS Chromosorb W (80–100 mesh) or 2.5% Silicone gum rubber E 301 on AW-DMCS Chromosorb G (80–100 mesh). I.r. spectra were recorded on a Perkin-Elmer 257 grating infrared spectrometer.

**Addition of Chlorine to the Diene (1).**—(a) A solution of the diene (1)<sup>2</sup> (1.0 g, 0.003 mol) in carbon tetrachloride (50 ml), to which disodium hydrogen orthophosphate (0.1 g) was added, was deoxygenated by the passage of nitrogen

gas for 30 min. Chlorine gas dried by passage through concentrated  $H_2SO_4$  and then over granulated calcium chloride was then bubbled through the boiling solution for 3 h. The cooled reaction mixture was then poured into water (50 ml), and extracted with carbon tetrachloride ( $3 \times 50$  ml); the combined extracts were then dried ( $MgSO_4$ ), filtered, and the filtrate evaporated *in vacuo*. The residue (1.2 g) was then analysed by g.l.c. and n.m.r., and the results are given in Table 1. Column chromatography using silica gel (Fisons 100–200 mesh) and light petroleum (b.p. 40–60 °C) as eluant permitted successive isolation of the following chlorides: (i) 1,2,3,4,5-endo,6-endo,7,7-octachloro-5-exo-methylnorborn-2-ene (5A) (0.2 g), m.p. 144–145 °C (from methanol) (Found: C, 25.3; H, 1.3.  $C_8H_4Cl_8$  requires C, 25.0; H, 1.05%);  $\nu_{max}$  ( $cm^{-1}$ ) 1 610 (*cis*-ClC=CCl); (ii) 1,2,3,4,5-exo,6-exo,7,7-octachloro-5-endo-methylnorborn-2-ene (6A) [admixed with an equal amount of (5A)] (0.35 g), m.p. 146–148 °C (after sublimation at 145–150 °C and 0.1 mmHg) (Found: C, 25.5; H, 1.2.  $C_8H_4Cl_8$  requires C, 25.0; H, 1.05%);  $\nu_{max}$  ( $cm^{-1}$ ) 1 613 (*cis*-ClC=CCl); (iii) 1,2,3,4,5-endo,6-exo,7,7-octachloro-5-exo-methylnorborn-2-ene (7A) [containing about 8% of (5A) and 23% of (6A)] (0.2 g), m.p. 147–148 °C (after sublimation at 145–150 °C and 0.1 mmHg) (Found: C, 25.7; H, 1.2.  $C_8H_4Cl_8$  requires C, 25.0; H, 1.05%);  $\nu_{max}$  ( $cm^{-1}$ ) 1 624 (*cis*-ClC=CCl); and (iv) 1,2,3,4,5-exo,6-endo,7,7-octachloro-5-endo-methylnorborn-2-ene (4A) (0.2 g), m.p. 176–177 °C (after sublimation at 145–150 °C and 0.1 mmHg) (Found: C, 25.6; H, 1.3.  $C_8H_4Cl_8$  requires C, 25.0; H, 1.05%);  $\nu_{max}$  ( $cm^{-1}$ ) 1 609 (*cis*-ClC=CCl).

It was possible to crystallise from the reaction mixture, using methanol, a white crystalline solid, m.p. 128–135 °C (Found: C, 20.1; H, 0.4; Cl, 78.6%. Mass spectrum suggested species  $C_8HCl_{13}$ ,  $C_8H_2Cl_{12}$ ,  $C_8HCl_{11}$ , and  $C_8Cl_{12}$ ).

(b) When acetic acid (20 ml) to which sulphuric acid (0.4 g) was added, was used as solvent, and the reaction mixture heated at 90° for 4 h, the sole product was 1,2,3,4,6-endo,7,7-heptachloro-5-methylenenorborn-2-ene (10), m.p. 70–71 °C (Found: C, 27.8; H, 1.0.  $C_8H_3Cl_7$  requires C, 27.7; H, 0.9%);  $\delta$  (60 MHz,  $CCl_4$ ) 5.82 (t, H-8-*transoid*), 5.67 (t, H-8-*cisoid*), and 5.10 (t, H-6-*exo*);  $J_{8-transoid,8-cisoid}$  1.5 and  $J_{6-exo,8}$  1.8 Hz;  $\nu_{max}$  ( $cm^{-1}$ ) 1 604 (*cis*-ClC=CCl).

(c) The diene (1) (1.0 g, 0.003 mol) and oxalyl chloride (4.0 g, 0.031 mol) were irradiated with a Hanovia 450-W u.v.s. medium-pressure lamp for 25 h under an atmosphere of nitrogen. The excess of oxalyl chloride was removed by evaporation, and the residue (1.2 g) analysed by n.m.r. and g.l.c. The results are given in Table 1.

**Reaction of Octachloronorbornenes (4A)–(7A) with Base.**—Following a repeat of reaction (a), the product mixture (1.2 g) was treated with a solution of sodium hydroxide (1.0 g, 0.025 mol) in ethanol (20 ml) and stirred at room temperature for 12 h. The ethanol was evaporated off and the residue mixed with water (50 ml) and extracted with carbon tetrachloride ( $3 \times 50$  ml). The combined extracts were dried ( $MgSO_4$ ), filtered, and the filtrate concentrated *in vacuo*. G.l.c. and n.m.r. analysis of the reaction mixture showed the absence of (4A) and (6A); (7A) had not reacted and about 50% of (5A) was still present. This indicated the following order of reactivity towards base: (4A)  $\approx$  (6A)  $\gg$  (5A) < (7A).

**Addition of Bromine to the Diene (1).**—(a) The diene (1) (1.0 g, 0.0032 mol) and bromine (0.8 g, 0.005 mol) in carbon tetrachloride (20 ml) to which benzoyl peroxide (0.1 g) had been added were boiled at reflux for 24 h. The cooled re-

action mixture was then mixed with water (50 ml) and extracted with carbon tetrachloride ( $3 \times 50$  ml). The combined extracts were washed with saturated aqueous sodium hydrogencarbonate solution (50 ml) and then dried ( $\text{MgSO}_4$ ), filtered, and the filtrate concentrated *in vacuo*. The results of the g.l.c. and n.m.r. analysis of the reaction product are given in Table I. The reaction product mixture (1.5 g) was then chromatographed on neutral alumina (Woelm, activity grade I) using light petroleum (b.p. 40–60 °C) as eluant to afford successively: (i) 5-endo,6-endo-dibromo-1,2,3,4,7,7-hexachloro-5-exo-methylnorborn-2-ene (5B) (0.2 g), m.p. 190–192 °C (from methanol) (Found: C, 20.7; H, 0.9; Br, 34.1; Cl, 45.4.  $\text{C}_8\text{H}_4\text{Br}_2\text{Cl}_6$  requires C, 20.3; H, 0.85; Br, 33.8; Cl, 45.0%);  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 1 611 (*cis*-ClC=CCl); (ii) 5-exo,6-exo-dibromo-1,2,3,4,7,7-hexachloro-5-endo-methylnorborn-2-ene (6B) (0.1 g), m.p. 179–181 °C (from methanol) (Found: C, 20.5; H, 0.8; Br, 31.3; Cl, 44.3.  $\text{C}_8\text{H}_4\text{Br}_2\text{Cl}_6$  requires C, 20.3; H, 0.85; Br, 33.8; Cl, 45.0%);  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 1 612 (*cis*-ClC=CCl); (iii) 5-endo,6-exo-dibromo-1,2,3,4,7,7-hexachloro-5-exo-methylnorborn-2-ene (7B) (0.1 g), m.p. 166–168 °C (from methanol) (Found: C, 20.8; H, 1.3.  $\text{C}_8\text{H}_4\text{Br}_2\text{Cl}_6$  requires C, 20.3; H, 0.85%);  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 1 610 (*cis*-ClC=CCl); and (iv) 5-exo,6-endo-dibromo-1,2,3,4,7,7-hexachloro-5-endo-methylnorborn-2-ene (4A) (0.1 g), m.p. 157–158 °C (from methanol) (Found: C, 20.5; H, 1.1.  $\text{C}_8\text{H}_4\text{Br}_2\text{Cl}_6$

requires C, 20.3; H, 0.85%);  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 1 625 [*cis*-ClC=CCl).

(b) When acetic acid (20 ml) to which sulphuric acid (0.4 g) and quinol (0.1 g) were added was used as solvent and the reaction mixture heated at 90 °C for 3.5 h a similar product distribution was obtained. The results are summarised in Table I.

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