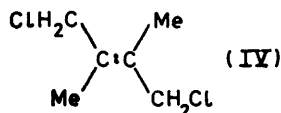
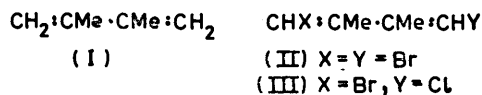


Organohalogen Compounds. Part II.¹ The Reactions of 2,3-Dimethylbuta-1,3-diene with Chlorine and with Iodine Monochloride

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The reaction of 2,3-dimethylbuta-1,3-diene with an equimolar amount of chlorine in carbon tetrachloride at -20°C gives mainly *trans*-1,4-dichloro-2,3-dimethylbut-2-ene and 2-chloromethyl-3-methylbuta-1,3-diene. Chlorination in methylene chloride at -78°C with gaseous chlorine yields initially a mixture of the same compounds and 1-chloro-2,3-dimethylbuta-1,3-diene in comparable amounts, together with the hydrogen chloride adducts 3-chloro-2,3-dimethylbut-1-ene and 1-chloro-2,3-dimethylbut-2-ene; further chlorination affords 1-chloro-3-chloromethyl-2-methylbuta-1,3-diene, 2,3-bis(chloromethyl)buta-1,3-diene, and 1,4-dichloro-2,3-bis(chloromethyl)but-2-ene and then a mixture of trichlorides, 1,2,3,4-tetrachloro-2-chloromethyl-3-methylbutane, and unidentified polychlorides. Bromination of *trans*-1,4-dichloro-2,3-dimethylbut-2-ene followed by dehydrobromination of the adduct gives 1,4-dichloro-2,3-dimethylbuta-1,3-diene in high yield. The reaction of 2,3-dimethylbuta-1,3-diene with iodine monochloride affords, as the only identified product, 1,2,3,4-tetrachloro-2,3-dimethylbutane.

THE bromination of 2,3-dimethylbuta-1,3-diene (I) has been reported previously¹⁻⁴ and certain of the products have been used as intermediates for the preparation of 1,4-dibromo- and 1-bromo-4-chloro-2,3-dimethylbuta-1,3-diene [(II) and (III)].¹



The chlorination of the diene (I) has been little investigated, although it has been reported⁵ that chlorination at -20° gave *trans*-1,4-dichloro-2,3-dimethylbut-2-ene (IV) (13%) as the only identified product.

Chlorination of the Diene (I).—The results of chlorination of the diene (I) (*ca.* 0.25 mol) with an equimolar amount of chlorine in carbon tetrachloride at -20°C and with gaseous chlorine (rate 0.10 mol h⁻¹) in solvent methylene chloride at -78°C or carbon tetrachloride at -20°C for various lengths of time (1–4 h) are shown in the Table. A further chlorination of diene (I), in solvent methylene chloride at -78°C and with gaseous chlorine (8 h), is discussed later because only one product (XI) isolated from this reaction is included in the Table.

It has been reported⁷ that the chlorination of isoprene in the dark in the liquid or gas phase at between -20 and 100°C involves ionic intermediates. Similar intermediates are probably involved in the chlorination of the diene (I) (comparable product distributions in reactions at -20 and -78°C and in reactions in the absence or presence of light), and all

Chlorination of 2,3-dimethylbuta-1,3-diene

Conditions	Solvent	Unchanged diene (%)	Products (%) in order of increasing g.l.c. retention time						
			(V) + (VI)	(VII)	(VIII)	(IX)	(X)	(IV)	(XI)
-20° , dark *	CCl ₄	75		54		1		45	
-20° , light *	CCl ₄	67		51		1		47	
-78° , 1 h †	CH ₂ Cl ₂	81	18	22	10	20		8	19
-78° , 2 h †	CH ₂ Cl ₂	52	18	Trace	31	Trace		22	20
-78° , 4 h †	CH ₂ Cl ₂	25	16		29			14	15
-20° , 2 h †	CCl ₄	<i>ca.</i> 83	23	Trace	34	Trace		21	19

* Chlorination with Cl₂-CCl₄. † Chlorination with gaseous chlorine. ‡ A mixture (*ca.* 12%) of two other components present (possibly trichloro-compounds on the basis of their g.l.c. retention times).

We have studied the chlorination of the diene (I) under two sets of conditions, to determine the initial chlorination and polychlorination products and to compare the results with those previously reported for the chlorination of isoprene.^{6,7} The reaction of the diene (I) with iodine monochloride has also been carried out.

¹ Part I, E. Z. Said and A. E. Tipping, *J.C.S. Perkin I*, 1972, 1399.

² E. H. Farmer, C. D. Lawrence, and W. D. Scott, *J. Chem. Soc.*, 1930, 510.

³ O. J. Sweeting and J. R. Johnson, *J. Amer. Chem. Soc.*, 1946, **68**, 1057.

⁴ A. You-lan Yao Ku, Ph.D. Thesis, University of Texas, 1962.

the products shown in the Table can be rationalised in terms of ionic addition of chlorine and hydrogen chloride and substitutive ionic chlorination.

The hydrogen chloride adducts (V) and (VI) were identified by comparison of their ¹H n.m.r. spectra with those of authentic samples prepared by reaction of the diene (I) with hydrogen chloride. Compounds (VII), (X), and (XI) were isolated pure and their

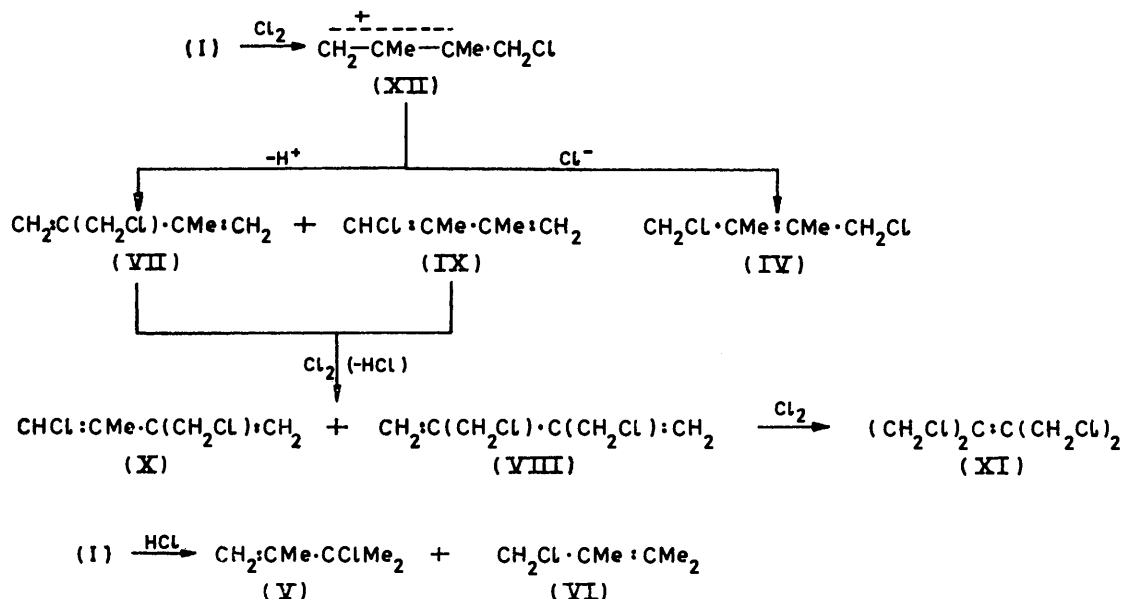
⁵ H. M. Hellman, J. W. Hellman, and K. Mislow, *J. Amer. Chem. Soc.*, 1954, **76**, 1175.

⁶ E. G. E. Hawkins and M. D. Philpot, *J. Chem. Soc.*, 1962, 3204.

⁷ G. D. Jones, W. B. Tefertiller, C. F. Raley, and J. R. Runyon, *J. Org. Chem.*, 1968, **33**, 2946.

structures were determined from their i.r., mass, and n.m.r. spectra. The tetrachloride (XI) reacted with bromine to afford the dibromide $(\text{CH}_2\text{Cl})_2\text{CBr}\cdot\text{CBr}\cdot(\text{CH}_2\text{Cl})_2$ (80%). The dienes (VIII) and (IX) could not be obtained absolutely pure by g.l.c. The former was

reaction (1 h) of the hydrogen chloride adducts (V) and (VI) and an appreciable amount of the diene (IX) (20%) [which requires loss of one of the more acidic hydrogen atoms in intermediate (XII) as a proton, *i.e.* one in the CH_2Cl group rather than the methyl group],

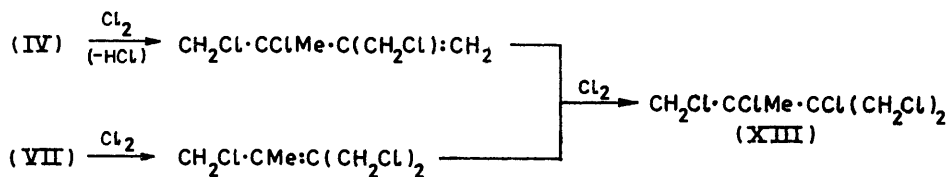


identified by n.m.r. spectroscopy and by treatment of the impure material with bromine to afford *trans*-1,4-dibromo-2,3-bis(chloromethyl)but-2-ene, $[\text{CH}_2\text{Br}\cdot\text{C}(\text{CH}_2\text{Cl})\text{C}(\text{CH}_2\text{Cl})\cdot\text{CH}_2\text{Br}]$ (>90%); the latter was identified by its i.r. $[\lambda_{\text{max}} 6.20 \text{ and } 6.32 \mu\text{m} (\text{conj. C:C str.})]$, mass $[m/e 116 \text{ and } 118 (70\%, M^+)]$, and n.m.r. $[\tau 3.80 (\text{:CHCl}), 4.92 \text{ and } 5.00 (\text{H}_a \text{ and } \text{H}_b \text{ in } \text{:CH}_a\text{H}_b), 8.15 (\text{Me}), \text{ and } 8.22 (\text{Me})]$ spectra.

The results of the chlorination of the diene (I) under both sets of conditions compare favourably with those reported for the chlorination of isoprene under comparable conditions. Thus the reaction of isoprene with a solution of chlorine in carbon tetrachloride or chloroform⁶ gave, as the initial products, mainly 2-chloro-

suggest that the conditions are more polar in the reaction involving gaseous chlorine.

The 8 h chlorination reaction gave minor amounts of certain compounds obtained from the other chlorinations, the tetrachloride (XI) (*ca.* 8%), and at least eight components with longer g.l.c. retention times. Attempted separation of a sample of the mixture by liquid-phase chromatography followed by distillation of certain of the resultant fractions under reduced pressure gave the tetrachloride (XI) (5%) and 1,2,3,4-tetrachloro-2-chloromethyl-3-methylbutane (XIII) (29%) as the only identified products. The pentachloride (XIII) is probably formed by further chlorination of the dichloride (IV) and/or the diene (VII), *i.e.*



methylbuta-1,3-diene and *trans*-1,4-dichloro-2-methylbut-2-ene; the reaction with gaseous chlorine at -20°C in solvent chloroform⁷ gave the same products, together with a mixture of hydrogen chloride adducts and 1-chloro-2-methylbuta-1,3-diene (*ca.* 15%).

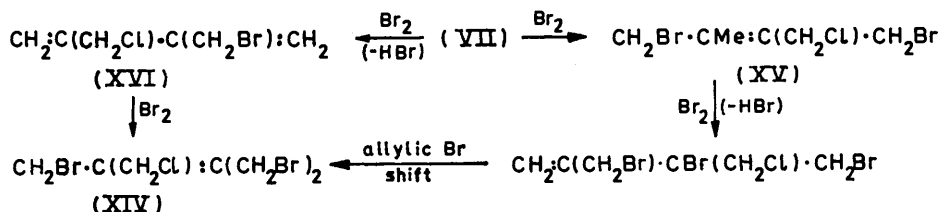
The differences in the products formed from comparable chlorinations of the diene (I) under the two sets of conditions (chlorine in carbon tetrachloride and gaseous chlorine), *i.e.* formation in the gaseous chlorine

Two of the expected products of the chlorination of the diene (I), 3,4-dichloro-2,3-dimethylbut-1-ene and 1,2,3,4-tetrachloro-2,3-dimethylbutane (XIX) were, perhaps surprisingly, not observed, although the former was probably initially formed and rearranged under the reaction conditions to the thermodynamically more stable *trans*-1,4-dichloride (IV).

The diene (VII) reacted with maleic anhydride at 30°C to afford the expected Diels-Alder adduct and with

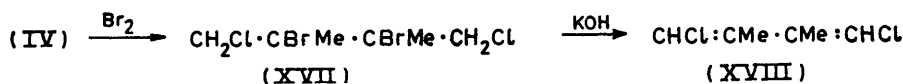
bromine at -78°C in carbon tetrachloride to give 1,4-dibromo-2-bromomethyl-3-chloromethylbut-2-ene (XIV) (47%) and a liquid which contained 1,4-dibromo-2-chloromethyl-3-methylbut-2-ene (XV) [n.m.r. bands at τ 8.05 (Me) and 6.00, 5.92, and 5.87 (CH_2Cl and $2 \times \text{CH}_2\text{Br}$)].

The substitution product (XIV) was unexpected because the reaction of the diene (I) with excess of bromine gave addition products only.¹ It probably arises *via* the intermediate formation of 2-bromo-methyl-2-chloromethylbuta-1,3-diene (XVI) and/or the dibromide (XV).



The reaction of the 1,4-dichloride (IV) with bromine in solvent methylene chloride gave 2,3-dibromo-1,4-dichloro-2,3-dimethylbutane (XVII) (93%), which on dehydrobromination with powdered potassium hydroxide *in vacuo* afforded 1,4-dichloro-2,3-dimethylbuta-1,3-diene (XVIII) (96%).

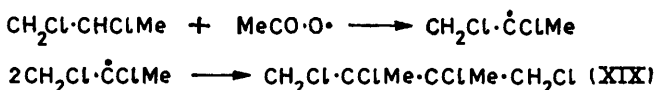
Reaction of the Diene (I) with Iodine Monochloride.—The reaction of iodine monochloride with the diene (I) (1:1 molar ratio) in solvent methylene chloride at -78°C gave polymeric material and the tetrachloride (XIX) (10%), present as a solid mixture of two isomers



(n.m.r. ratio 4:1), but it was not possible to determine unambiguously which was the *meso*- and which the (\pm)-isomer.

The 1,4-dichloride (IV) was not an intermediate in the formation of the tetrachloride (XIX), since the reaction of compound (IV) with iodine monochloride under comparable conditions gave polymeric material only.

The thermal decomposition of acetyl peroxide in 1,2-dichloropropane has been reported⁸ to afford a liquid product fraction which gave a correct chlorine analysis and molecular weight for the tetrachloride (XIX); the results of subsequent dehydrohalogenation followed by chemical degradation supported the assignment. This reaction has been repeated and, in contrast to the earlier report, gave a liquid mixture of at least eleven main components (g.l.c.), from which a solid mixture (2%) of the *meso*- and (\pm)-isomers of the tetrachloride (XIX) was isolated on cooling.



EXPERIMENTAL

The techniques used were as described previously¹ except that for g.l.c. a Pye 104 instrument was employed with columns (2 or 4 m) packed with Apiezon L grease (APL) or polyethylene glycol adipate (PEGA) (10% by weight) on Celite.

Chlorination of 2,3-Dimethylbutadiene.—(a) *With chlorine in carbon tetrachloride.* A saturated solution of chlorine (19.9 g, 0.28 mol) in carbon tetrachloride (100 ml) was added dropwise (2 h) to a solution of the diene (21.50 g, 0.262 mol) in carbon tetrachloride (100 ml) in the dark at -20°C . The product mixture was examined by g.l.c. (2 m APL at 75 – 160°C) and shown to contain unchanged diene (16.20 g,

0.196 mol, 75% recovered), 2-chloromethyl-3-methylbuta-1,3-diene (4.22 g, 36.0 mmol, 54%), *trans*-1,4-dichloro-2,3-dimethylbut-2-ene (4.57 g, 29.4 mmol, 45%), and 1-chloro-2,3-dimethylbuta-1,3-diene (0.07 g, 0.6 mmol, 1%). The solvent and the unchanged diene were removed by distillation under reduced pressure at 30°C ; g.l.c. analysis showed the presence of unchanged diene (15.30 g, 0.186 mol, 71% recovered) and 2-chloromethyl-3-methylbuta-1,3-diene (1.12 g, 9.60 mmol, 15%). Distillation of the residue (9.80 g) under reduced pressure through an efficient column in the presence of a trace of hydroquinone, gave (i) a mixture (2.80 g), b.p. 20° at 9 mmHg, shown by g.l.c.

(as before) to contain unchanged diene (0.80 g, 9.75 mmol, 4% recovered), 2-chloromethyl-3-methylbuta-1,3-diene (0.59 g, 5.10 mmol, 8%), and carbon tetrachloride (1.41 g), (ii) 2-chloromethyl-3-methylbuta-1,3-diene (1.30 g, 11.16 mmol, 17%) [Found: Cl, 30.2%; *M* (mass spec.), 116.5. $\text{C}_6\text{H}_9\text{Cl}$ requires Cl, 30.4%; *M*, 116.5], b.p. 25 – 27° at 9 mmHg; λ_{max} (hexane) 223–224 nm (ϵ 12,250); λ_{max} 6.14 μm and 6.24 vs μm (conj. C:C str.); *m/e* 118 and 116 (M^+ , 80%) and 81 [$(M - \text{Cl})^+$, 100%]; τ 3.70, 3.78, 3.81, and 3.94 (total 4H, vinylic H), 5.80 (2H, CH_2Cl), and 8.10 (3H, Me), (iii) *trans*-1,4-dichloro-2,3-dimethylbut-2-ene (3.20 g, 20.92 mmol, 31%), m.p. 32 – 33° (lit.,⁵ 32 – 34°), b.p. 70 – 71° at 10 mmHg, i.r. spectrum identical with that reported,⁵ and (iv) a black liquid residue (1.70 g) which was not investigated further.

A second experiment carried out in light at -20°C gave unchanged diene (67%), 2-chloromethyl-3-methylbuta-1,3-diene (51%), *trans*-1,4-dichloro-2,3-dimethylbut-2-ene (47%), and 1-chloro-2,3-dimethylbuta-1,3-diene (1%).

(b) *With gaseous chlorine, experiment 1.* Chlorine gas (rate ca. 0.10 mol h^{-1}) was bubbled into a stirred solution of the diene (20.0 g, 0.244 mol) in methylene chloride (300 ml) at -78°C (1 h); hydrogen chloride was evolved during

⁸ M. S. Kharasch and G. Buchi, *J. Amer. Chem. Soc.*, 1951, **73**, 632.

the reaction. The solvent and the unchanged diene were distilled off under reduced pressure and g.l.c. (2m PEGA at 70 °C) showed the presence of unchanged diene (15.1 g, 0.184 mol, 79% recovered). The residue (7.3 g) was shown by g.l.c. (2 m APL at 160 °C) to contain eight components (A—H) present in the ratios 7 : 6 : 11 : 21 : 10 : 19 : 8 : 18, together with traces of three components with longer retention times (*ca.* 1% of fraction). Separation of the components by g.l.c. (4 m APL at 160 °C) gave (i) unchanged diene (A) (0.33 g, 4.1 mmol, 2% recovered), (ii) a mixture (1.2 g, 9.9 mmol, 18%) (Found: M , 119. Calc. for $C_6H_{11}Cl$: M , 118.5) of the hydrogen chloride adducts 3-chloro-2,3-dimethylbut-1-ene (B) (0.4 g, 3.5 mmol, 6%), τ 5.00 (1H, s, vinylic H_a), 5.10 (1H, q, vinylic H_b , $J_{b,Me}$ 1.0 Hz), 8.08 (3H, d, Me), and 8.20 (6H, s, Me_2C), and 1-chloro-2,3-dimethylbut-2-ene (C) (0.8 g, 6.4 mmol, 12%), τ 5.97 (2H, s, CH_2Cl), 8.25 (3H, s, Me), and 8.30 (6H, s, Me_2C), with n.m.r. spectra and g.l.c. retention times identical with those of authentic samples prepared by the reaction of hydrogen chloride with the diene, (iii) 2-chloromethyl-3-methylbuta-1,3-diene (D) (1.4 g, 12.2 mmol, 22%), (iv) 2,3-bis(chloromethyl)buta-1,3-diene (E) (0.9 g, 5.8 mmol, 10%), τ 4.48 and 4.58 (2H, H_a and H_b in $:CH_2H_b$) and 5.77 (2H, CH_2Cl), which could not be obtained absolutely pure, but which was identified by treating a sample (0.33 g, 2.2 mmol) with a solution of bromine in carbon tetrachloride until a slight bromine colour persisted in solution and then removing the solvent to give colourless needles of *trans*-1,4-dibromo-2,3-bis(chloromethyl)but-2-ene (0.62 g, 2.0 mmol, 92%) [Found: C, 23.4; H, 2.8; Br, 51.4; Cl, 22.7%; M (mass spec.), 311. $C_6H_8Br_2Cl_2$ requires C, 23.2; H, 2.6; Br, 51.3; Cl, 22.8%; M , 311]; λ_{max} 3.45 μ (C—H str.), 6.88s, 6.98s, 7.95vs, 8.05s, 8.30vs, 8.40s, 11.15m, 11.44m, 11.58s, 13.20s, 13.80m, 14.02s, 14.20s, 15.14m, and 15.80s μ m; m/e 316, 314, 312, 310, and 308 (M^+ , 16%), 279, 277, 275, and 273 [$(M - Cl)^+$, 12%], 235, 233, 231, and 229 [$(M - Br)^+$, 72%], 197, 195, and 193 ($C_6H_7BrCl^+$, 46%), 153, 151, and 149 ($C_6H_7Cl_2^+$, 100%), 103 and 101 ($C_6H_5Cl^+$, 16%), and 58 and 57 ($C_6H_5Cl^{2+}$, 6%); τ 5.30 (2H, CH_2Cl) and 5.90 (2H, CH_2Br), (v) 1-chloro-2,3-dimethylbuta-1,3-diene (F) (1.3 g, 11.1 mmol, 20%), λ_{max} 6.20s and 6.30m (conj. C:C str.), 9.50s, 10.90vs, 12.50m, 13.28s, and 13.75vs μ m, which could not be obtained absolutely pure but which was identified by 1H n.m.r. spectroscopy, (vi) 1-chloro-3-chloromethyl-2-methylbuta-1,3-diene (G) (0.7 g, 4.65 mmol, 8%) (Found: C, 47.5; H, 5.5. $C_6H_8Cl_2$ requires C, 47.7; H, 5.3%), λ_{max} 3.25m and 3.50m (C—H str.), 6.20m and 6.30m (conj. C:C str.), 9.50s, 10.00m, 11.02vs, 12.30m, 12.58s, 12.65m, 13.30m, and 13.80vs μ m; τ 3.80 (1H, $:CHCl$), 4.67 and 4.77 (2H, H_a and H_b in $:CH_2H_b$), 5.92 (2H, CH_2Cl), and 8.03 (3H, Me), and (vii) *trans*-1,4-dichloro-2,3-dimethylbut-2-ene (H) (1.6 g, 10.5 mmol, 19%).

(c) *With gaseous chlorine, experiment 2.* The reaction of chlorine gas with the diene under the same conditions as experiment 1, but for 2 h, gave unchanged diene (10.3 g, 0.126 mol, 52% recovered) and a higher-boiling residue (16.5 g) shown by g.l.c. (as before) to contain (i) a mixture (2.5 g, 21.1 mmol, 18%) of the hydrogen chloride adducts (B) and (C), (ii) 2,3-bis(chloromethyl)buta-1,3-diene (E) (5.5 g, 36.6 mmol, 31%), (iii) 1-chloro-3-chloromethyl-2-methylbuta-1,3-diene (G) (3.9 g, 25.5 mmol, 22%), (iv) *trans*-1,4-dichloro-2,3-dimethylbut-2-ene (H) (3.6 g, 23.3 mmol, 20%), and (v) a component (L) later identified as 1,4-dichloro-2,3-bis(chloromethyl)but-2-ene (0.9 g, 4.1

mmol, 4%) and present in the ratios 11 : 8 : 33 : 23 : 21 : 4, together with trace amounts of components (D) and (F) and two components with longer retention times.

Attempted separation of a sample (5.0 g) of the high-boiling residue by fractional distillation gave no separation into fractions of narrow b.p. range, and dehydrochlorination occurred. A second attempted separation of a sample (10.0 g) as a solution in light petroleum (b.p. 40—60°; 10 ml) by liquid-phase chromatography [activated alumina support, type H (100—200 mesh)] gave three fractions. The first (eluted with light petroleum) was treated with bromine until a slight bromine colour persisted in solution and the solvent was removed to afford crystals of *trans*-1,4-dibromo-2,3-bis(chloromethyl)but-2-ene (2.6 g, 8.4 mmol, 7%) and a dense yellow liquid (1.1 g). The second fraction (eluted with light petroleum), after removal of the solvent, gave a yellow dense liquid (3.3 g) which partially solidified at 0 °C and was shown by i.r. spectroscopy to contain *trans*-1,4-dichloro-2,3-dimethylbut-2-ene (H) and 1-chloro-3-chloromethyl-2-methylbuta-1,3-diene (G). The third fraction (eluted with benzene), after removal of the solvent, gave a mixture of solid and dense liquid. The solid was identified as 1,4-dichloro-2,3-bis(chloromethyl)but-2-ene (0.70 g, 3.2 mmol, 3%) [Found: C, 32.8; H, 3.6; Cl, 63.5%; M (mass spec.), 222. $C_6H_8Cl_4$ requires C, 32.4; H, 3.6; Cl, 63.9%; M , 222], m.p. 106—108°; λ_{max} 6.83s, 7.90s, 7.95s, 11.15m, 11.37vs, 11.46s, 13.72vs, and 14.50s μ m; λ_{max} (hexane) 224 nm (ϵ 10,400); m/e 228, 226, 224, 222, and 220 (M^+ , 93%), 191, 189, 187, and 185 [$(M - Cl)^+$, 31%], 190, 188, 186, and 184 [$(M - HCl)^+$, 100%], 177, 175, 173, and 171 ($C_5H_6Cl_3^+$, 81%), 164, 162, 160, and 158 ($C_4H_5Cl_3^+$, 28%), 153, 151, and 149 ($C_6H_7Cl_2^+$, 61%), 141, 139, and 137 ($C_5H_7Cl_2^+$, 30%), 127, 125, and 123 ($C_4H_5Cl_2^+$, 37%), 103 and 101 ($C_5H_6Cl^+$, 25%), and 89 and 87 ($C_4H_4Cl^+$, 28%); τ 5.74.

(d) *With gaseous chlorine, experiment 3.* The reaction of the diene with chlorine gas under similar conditions to those in experiment 1 (4 h) gave unchanged diene (5.4 g, 65.7 mmol, 26% recovered) and higher-boiling material (26.2 g) shown by g.l.c. (as before) to contain (i) a mixture (3.4 g, 29.1 mmol, 16%) of the hydrogen chloride adducts (B) and (C), (ii) 2,3-bis(chloromethyl)buta-1,3-diene (E) (7.75 g, 51.3 mmol, 29%), (iii) 1-chloro-3-chloromethyl-2-methylbuta-1,3-diene (G) (3.9 g, 25.6 mmol, 14%), (iv) the *trans*-1,4-dichloride (H) (4.2 g, 27.4 mmol, 15%), (v) a mixture (*ca.* 3.8 g, *ca.* 20.5 mmol, *ca.* 12%) of two components (J) and (K) considered to be trichloro-compounds, and (vi) 1,4-dichloro-2,3-bis(chloromethyl)but-2-ene (L) (3.0 g, 13.7 mmol, 8%), present in the ratios 7 : 10 : 30 : 15 : 16 : 5 : 7 : 8 (g.l.c.).

(e) *With gaseous chlorine, experiment 4.* The reaction of the diene with chlorine gas under similar conditions to those in experiment 1 (8 h), gave, after removal of the solvent, a yellow dense liquid (58.0 g) which was shown by g.l.c. (as before) to contain at least eight components (ratios *ca.* 1 : 3 : 2 : 6 : 7 : 23 : 25 : 33); a number of the peaks were incompletely resolved multi-component mixtures. Various methods were investigated in an attempt to separate the mixture and the most successful is described.

A sample of the mixture (15.0 g) was dissolved in light petroleum (b.p. 40—60°; 50 ml) and eluted from an alumina column with light petroleum to afford three liquid fractions (13.0 g). Further elution, with chloroform, gave the tetrachloride (L) [0.65 g, 2.9 mmol, 1% (5% yield

based on total product)]. The liquid fractions were combined and distilled under reduced pressure to afford (i) a fraction (8.3 g), b.p. 90–106° at 0.6 mmHg; λ_{\max} 215–216 nm, the n.m.r. spectrum of which showed the presence of methyl, methylene, and vinylic protons, and (ii) a residue identified as 1,2,3,4-tetrachloro-2-chloromethyl-3-methylbutane [4.7 g, 18.1 mmol, 7% (29% total yield)] [Found: C, 27.8; H, 3.3; Cl, 69.0%; M (mass spec.), 258.5. $C_6H_9Cl_5$ requires C, 27.8; H, 3.4; Cl, 68.7%; M , 258.5; λ_{\max} 7.00vs, 7.24vs, 7.77vs, 8.05s, 9.50s, 10.46s, 11.41s, 12.80vs, and 13.87vs μ m; τ 5.65 (2H, CH_2Cl), 5.73 (2H, CH_2Cl), 5.80 and 5.90 (2H, H_a and H_b in $CH_3H_bCl-CClMe^-$), and 8.05 (3H, Me).

(f) *With gaseous chlorine, experiment 5.* Chlorine gas was bubbled, at the same rate as in the previous experiments, into a stirred solution of the diene (20.0 g, 0.24 mol) in carbon tetrachloride (300 ml) at $-20^\circ C$ (2 h) to give (i) unchanged diene (ca. 83%), (ii) the hydrogen chloride adducts (B) and (C), the dichlorobuta-1,3-dienes (E) and (G), and the *trans*-1,4-dichloride (H) in the ratios 12:11:34:21:19 (g.l.c.), together with traces of the dienes (D) and (F) and two components with much longer g.l.c. retention times.

Reaction of 2,3-Dimethylbuta-1,3-diene with Iodine Monochloride.—A solution of iodine monochloride (32.0 g, 0.19 mol) in methylene chloride (250 ml), added dropwise (2.5 h) to a well stirred solution of the diene (16.2 g, 0.19 mol) in methylene chloride (175 ml) at $-78^\circ C$, gave initially a yellow precipitate and a dark yellow lachrymatory liquid, which on warming to room temperature formed a dark brown solution. Removal of solvent under reduced pressure gave a dark green solution which, on treatment with aqueous sodium thiosulphate (to remove iodine), afforded a yellow-brown solution. This solution was extracted with ether, washed with water, dried ($CaCl_2$), and evaporated (under reduced pressure), and the resultant dense liquid (26.5 g) was distilled under reduced pressure to give (i) a yellow liquid (0.85 g), b.p. 25° at 1.0 mmHg; λ_{\max} 3.38s, 3.42m, and 3.49s (C–H str.), 6.20w (C–C str.), 6.90s, 7.35s, 7.93s, 11.37s, 12.26vs, and 13.88s μ m; τ (15% solution in CCl_4) 3.00 (4H, d, J 2.0 Hz), 5.24 (3H, s), 7.80 (8H, d, J 2.0 Hz), and 8.73 (12H, s), (ii) a yellow liquid (8.2 g), b.p. 65–70° at 1.5–2.0 mmHg, which partially solidified to afford crystals of 1,2,3,4-tetrachloro-2,3-dimethylbutane (4.7 g, 21.2 mmol, 10%) (Found: C, 32.4; H, 4.6; Cl, 63.2. $C_6H_{10}Cl_4$ requires C, 32.2; H, 4.5; Cl, 63.3%), m.p. (capillary) 96–98°; λ_{\max} 3.42vs and 3.50s (C–H str.), 6.90s, 7.03s, 7.26vs, 9.65vs, 11.15s, 11.45s, and 13.28vs μ m; m/e 115, 113, and 111 ($C_3H_5Cl_2^+$, 30%) and 78 and 76 ($C_3H_5Cl^+$, 100%); τ (15% solution in CCl_4 for $CH_3H_bCl-CClMe-CClMe-CH_3H_bCl$, present as two isomers in ratio 4:1) 5.83 (2H, d, J_{ab} 12.0 Hz), 6.03 (2H, dq, H_b , $J_{b,Me}$ 0.6 Hz) and 8.15 (6H, d, Me) for major isomer and 5.90 (2H, d, H_a , J_{ab} 11.8 Hz), 6.09 (2H, dq, H_b , $J_{b,Me}$ 0.5 Hz), and 8.10 (6H, d, Me) for minor isomer; the filtrate (3.2 g) changed slowly to a dark brown liquid, (iii) a deep green liquid (2.8 g), b.p. 100–108° at 3.0 mmHg, which in air solidified to a dark green solid (Found: C, 49.6; H, 6.7%), m.p. 60–63° C, and (iv) a dark brown polymeric residue (12.2 g).

Reaction of Acetyl Peroxide with 1,2-Dichloropropane.—A solution of acetyl peroxide (16.8 g, 0.14 mol) in 1,2-dichloropropane (40.0 g, 0.36 mol) was added dropwise to an excess of the dichloropropane (63.0 g, 0.56 mol) at 80° C (2 h) and the mixture was refluxed (1 h). The volatile material

(mostly unchanged dichloropropane) was removed by distillation to leave a residue (12.0 g) which, on distillation under reduced pressure, afforded (i) a colourless liquid (0.70 g) (Found: C, 37.0; H, 4.9; Cl, 57.8%), b.p. 55–65° 0.06 mmHg, (ii) a dense liquid (0.6 g), b.p. 65–70° at 0.06 mmHg, (iii) a dense liquid (1.7 g), b.p. 85–95° at 0.15 mmHg, (iv) a black residue (3.5 g), and (v) a volatile lachrymatory liquid (4.2 g) which collected in the cold trap and which was shown by 1H n.m.r. spectroscopy to be a mixture of unchanged dichloropropane, methyl acetate, acetic acid, and 1,2,2-trichloropropane.

Fractions (i)–(iii) were cooled to $-5^\circ C$ (ca. 3 days) at which temperature fractions (ii) and (iii) deposited colourless needles of a mixture of *meso*- and (\pm)-1,2,3,4-tetrachloro-2,3-dimethylbutane (0.7 g, 3.1 mmol, 2%). Fraction (i) and the filtrates from fractions (ii) and (iii) (total 2.3 g) had identical i.r. and n.m.r. spectra and g.l.c. showed the presence of eleven major and several minor components.

Reactions of 2-Chloromethyl-3-methylbuta-1,3-diene.—(a) *With bromine.* A solution of bromine (2.10 g, 13.10 mmol) in methylene chloride (10 ml) was added dropwise (5 min) to a stirred solution of the diene (0.45 g, 3.86 mmol) in methylene chloride (10 ml) at $-78^\circ C$. The solvent was removed under reduced pressure at room temperature, the resultant material was cooled at 0° C (2 h), the precipitate was filtered off and washed with carbon tetrachloride to afford colourless crystals of 1,4-dibromo-2-bromomethyl-3-chloromethylbut-2-ene (0.54 g, 1.83 mmol, 47%) [Found: C, 20.5; H, 2.5; Br, 67.8; Cl, 9.8%; M (mass spec.), 355.5. $C_6H_8Br_3Cl$ requires C, 20.3; H, 2.3; Br, 67.6; Cl, 10.0%; M , 355.5], m.p. (capillary) 136–138°; λ_{\max} 3.43s (dbl) and 3.50m (C–H str.), 6.85vs, 6.97s, 7.27s, 8.32vs, 8.40s, 11.30s, 11.60s, 13.20vs, and 14.60vs μ m; m/e 360, 358, 356, 354, and 352 (M^+ , 21%), 279, 277, 275, and 273 [$(M - Br)^+$, 100%], 197, 195, and 193 ($C_6H_7BrCl^+$, 77%), 117 and 115 ($C_6H_8Cl^+$, 54%), and 91 and 89 ($C_4H_8Cl^+$, 11%). The dense filtrate (ca. 0.4 g) was shown by i.r. spectroscopy to contain unsaturated components (bands at 5.5–6.2 μ m) and the n.m.r. spectrum (30% solution in CCl_4) showed the presence of 1,4-dibromo-2-chloromethyl-3-methylbut-2-ene.

(b) *With maleic anhydride.* A well stirred solution of the diene (2.40 g, 20.60 mmol) in excess of maleic anhydride (1.50 g, 0.15 mol) was heated at 30° C (1 h). The mixture was treated with water (5×25 ml) and the solid residue filtered to give colourless crystals of 4-chloromethyl-5-methylcyclohex-4-ene-1,2-dicarboxylic acid (4.22 g, 17.70 mmol, 86%) (Found: C, 51.6; H, 6.1; Cl, 15.6. $C_{10}H_{13}ClO_4$ requires C, 51.5; H, 5.7; Cl, 15.3%), m.p. 134–136°; λ_{\max} 3.45s, 5.42s, 5.60s, 5.82vs, 6.98vs, 7.48s, 7.76s, 7.95s, 8.50s, 9.05s, 9.50s, 10.05s, 10.45s, 10.70s, 11.60s, 12.70vs, 14.00s, 14.20s, and 14.55vs μ m.

Reactions of trans-1,4-Dichloro-2,3-dimethylbut-2-ene.—(a) *With iodine monochloride.* A solution of iodine monochloride (3.1 g, 19.1 mmol) in methylene chloride (30 ml) was added dropwise to a well stirred solution of the dichloride (2.8 g, 18.3 mmol) in methylene chloride (50 ml) at $-78^\circ C$. Removal of the solvent gave a dark green liquid which was washed with aqueous sodium thiosulphate and extracted with ether to afford a liquid polymer (2.1 g), which was unsaturated (λ_{\max} 6.20 μ m).

(b) *With bromine.* A mixture of the dichloride (2.0 g, 13.1 mmol), lithium bromide (0.10 g), hydroquinone (trace), and bromine (2.80 g, 17.4 mmol) in methylene chloride (80 ml) was refluxed (1.5 h) to give, after removal of the

solvent under reduced pressure, 2,3-dibromo-1,4-dichloro-2,3-dimethylbutane (3.9 g, 12.4 mmol, 93%) (Found: C, 23.3; H, 3.2; Br, 51.0; Cl, 22.9. $C_6H_{10}Br_2Cl_2$ requires C, 23.0; H, 3.2; Br, 51.1; Cl, 22.7%), m.p. 109–110 °C; λ_{max} 3.39 and 3.42m (C–H str.), 7.05s, 7.28vs, 7.75s, 9.23s, 9.73s, 11.15s, and 13.30vs μm ; m/e 237, 235, 233, and 231 [$(M - Br)^+$, 100%], 199, 197, and 195 ($C_6H_9BrCl^+$, 74%), 185, 183, and 181 ($C_5H_7BrCl^+$, 27%), 159, 157, and 155 ($C_3H_5BrCl^+$, 68%), 155, 153, and 151 ($C_6H_9Cl_2^+$, 79%), 125, 123, and 121 ($C_4H_3Cl_2^+$, 41%), and 105 and 103 ($C_5H_8Cl^+$, 32%); τ (10% solution in CCl_4 for $CH_aH_bCl \cdot CBrMe \cdot CBrMe \cdot CHHCl$) 5.72 (1H, d, H_a , J_{ab} 12.0 Hz), 5.93 (1H, dq, H_b , $J_{b,Me}$ 0.6 Hz), and 7.96 (3H, d, Me).

Preparation of 1,4-Dichloro-2,3-dimethylbuta-1,3-diene.—2,3-Dibromo-1,4-dichloro-2,3-dimethylbutane (0.75 g, 2.40 mmol) and an excess of dry, powdered potassium hydroxide (2.0 g), heated slowly *in vacuo* to 80 °C (3 h), gave 1,4-dichloro-2,3-dimethylbuta-1,3-diene (0.35 g, 2.30 mmol, 96%) [Found: C, 47.4; H, 5.3; Cl, 46.9%; M (mass spec.), 151. $C_6H_8Cl_2$ requires C, 47.7; H, 5.3; Cl, 47.0%; M , 151]; λ_{max} 3.25s, 3.38s, 3.42s, and 3.50m (C–H str.), 6.20s and 6.35s (conj. C:C str.), 6.95vs, 7.28vs, 7.60s, 7.93s, 9.10s,

9.25s, 9.45s, 9.50vs, 10.00s, 10.46s, 12.10s, 12.61vs, 12.79vs, 13.20s, and 13.95s μm ; λ_{max} (hexane) 234 (ϵ 5860) nm, λ_{inf} 239–242 (5390) and 248.5–250 nm (3350); m/e 154, 152, and 150 (M^+ , 100%) and 117 and 115 [$(M - Cl)^+$ 68%]; τ (for two isomers, present in ratio 3:2) 3.70 (complex, 1H, $\cdot CHCl$) and 8.05 (complex, 3H, Me); 3.83 (complex, 1H, $\cdot CHCl$) and 8.08 (complex, 3H, Me).

Reaction of 1,4-Dichloro-2,3-bis(chloromethyl)but-2-ene with Bromine.—A solution of the olefin (0.65 g, 2.9 mmol) and bromine (1.0 g, 6.2 mmol) in methylene chloride (50 ml) was refluxed (5 h) to give, after removal of solvent, colourless crystals of 2,3-dibromo-1,4-dichloro-2,3-bis(chloromethyl)butane (0.9 g, 2.3 mmol, 80%) (Found: C, 18.5; H, 2.4. $C_6H_8Br_2Cl_4$ requires C, 18.8; 2.1%), m.p. 147–149°; λ_{max} 6.87s, 8.34vs, 8.43s, 11.43vs, 11.56s, 14.60vs, and 15.14vs μm ; τ 5.88 (s, CH_2Cl).

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