# 618. *Chlorination of Isoprene.*

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Chlorination of isoprene, in an inert solvent, initially yields mainly 2-chloromethylbutadiene and 1,4-dichloro-2-methylbut-2-ene together with some 3,4-dichloro-3- and 3,4-dichloro-2-methylbut-1-ene. An excess of chlorine leads to the formation of a mixture of trichloropentenes, some of which have been identified, and 1,2,3,4-tetrachloro-2-methylbutane. Chlorination of the dichloropentenes with chlorine and with sulphuryl chloride, and dehydrochlorination of the trichloropentenes and tetrachloropentane, have been studied.

The chlorination of isoprene appears to have been little studied, except by Jones and Williams [1] and Tishchenko.[2] The former workers stated that reaction of the diene with a solution of chlorine in carbon tetrachloride yielded mainly 1-chloro-2-methylbutadiene (I) and 1,4-dichloro-2-methylbut-2-ene (III), together with small amounts of isomeric dichloropentenes and high-boiling residues. On the other hand, Tishchenko has claimed that the diene product was 2-chloromethylbutadiene (II), similar to that obtained, in unspecified yield, by chlorination of isoprene vapour in ultraviolet light.[3]

$$\text{(I)}\quad \mathrm{Cl{\cdot}CH{=}CMe{\cdot}CH{=}CH_2} \qquad \mathrm{CH_2{=}C(CH_2Cl){\cdot}CH{=}CH_2}\quad \text{(II)}$$

The evidence for structure (I) was based on (i) the ability of the diene to form, with sulphur dioxide, a cyclic sulphone from which the components could be regenerated on heating, and (ii) the isolation of a compound, m. p. 171—172° (corr.), reported to be 1-chloro-2-methylanthraquinone, by oxidation of the product of Diels–Alder reaction between the diene and 1,4-naphthaquinone. No mixed m. p. was quoted for this anthraquinone. Structure (II) was supported by the findings that (*a*) the diene had different properties from those of 1-chloro-2-methylbutadiene synthesised by an independent route, (*b*) the rate of reaction of the diene with alcoholic potassium hydroxide appeared to be more in line with that required for an allylic than a vinylic chlorine, and (*c*) oxidation with potassium permanganate provided chloroacetic acid.

In the present work it was confirmed (cf. ref. 1) that passage of gaseous chlorine directly into a solution of isoprene in carbon tetrachloride (or chloroform) gave rise to a greater proportion of polychlorinated products (particularly trichloropentenes) than when a solution of chlorine in carbon tetrachloride was used, and also that the major products were the above chloropentadiene and 1,4-dichloro-2-methylbut-2-ene. It was also confirmed that oxidation of the diene with permanganate yielded chloroacetic acid, and that it underwent a Diels–Alder reaction with 1,4-naphthaquinone very easily. However, attempts to oxidise the product of the latter reaction in alcoholic alkali, as described by Jones and Williams, proved unsatisfactory: the alkali obviously reacted with the solute, even at room temperature, and after prolonged treatment with air or oxygen a complex mixture was obtained from which the compound described by Jones and Williams was isolated in low yield by repeated recrystallisation. However, this oxidation stage was carried out smoothly and rapidly by use of chromium trioxide in acetic acid at *ca.* 60°, but the product, obtained in high yield, was found to be not 1-chloro-2-methylanthraquinone but 2-chloromethylanthraquinone, by comparison with the synthetic compounds (mixed m. p.s and infrared spectra). This evidence confirmed structure (II): use of ozonolysis led to a mixture of unstable products whose infrared spectrum was difficult to interpret. The *cis*- and *trans*-isomers of 1-chloro-2-methylbutadiene may have been present in a minor degree since gas-chromatography showed that, in addition to the main

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[1] Jones and Williams, *J.*, 1934, 829.

[2] Tishchenko, *Zhur. obshchei Khim.*, 1936, **6**, 1116; Tishchenko, Abramova, and Yarzhemskaya, *ibid.*, 1957, **27**, 227.

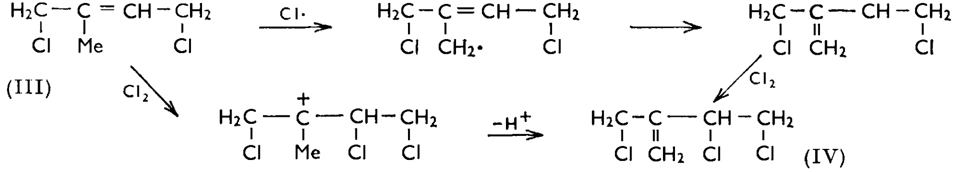
[3] Thiokol Chem. Corp., U.S.P. 2,937,125.

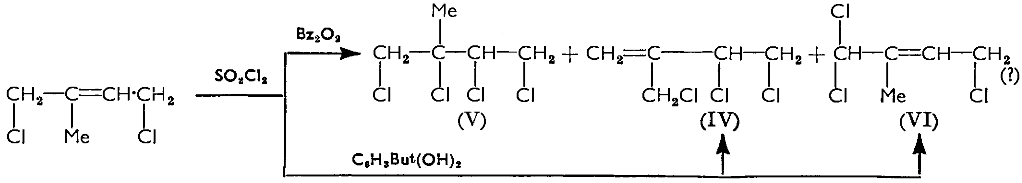
component (87%), there were two other substances (3% and 10%) in this fraction, the last containing a methyl group (band at 1379 cm.$^{-1}$).

Although the minor products from the chlorination of isoprene contained 3,4-dichloro-2-methylbut-1-ene, as proposed by Ultée,[4] who synthesised this compound, there was found to be a larger proportion of 3,4-dichloro-3-methylbut-1-ene. The higher-boiling products included 2,3,4-trichloro-3-methylbut-1-ene, 3,4-dichloro-2-chloromethylbut-1-ene, 1,4-dichloro-2-chloromethylbut-2-ene, a compound of uncertain structure (possibly 1,1,4-trichloro-2-methylbut-2-ene), and tetrachloropentanes. The structures of these olefins were based on the evidence from spectroscopy and ozonolysis, although, in agreement with Bailey *et al.*,[5] it was found that ozonolysis of polychloro-olefins was extremely slow.

The formation of 2-chloromethylbutadiene from isoprene evidently arises through substitutive chlorination in the allylic position. When the diene was ascribed structure (I) it was assumed that its production involved dehydrochlorination of a dichloropentene, but control experiments showed that, under normal chlorination conditions (of temperature, solvent, presence of hydrogen chloride and chlorine), 1,4-dichloro-2-methylbut-2-ene, 3,4-dichloro-2-methylbut-1-ene, and 3,4-dichloro-3-methylbut-1-ene were each recovered unchanged, hydrogen chloride not being lost in this way. The dichloropentenes must have arisen through the three possible modes of chlorine addition (1,4; 1,2; 3,4) with a preference for 1,4. However, part of the 3,4-dichloro-3-methylbut-1-ene could have been formed by addition of hydrogen chloride to 2-chloromethylbutadiene: experiments showed that such a reaction takes place when anhydrous hydrogen chloride is used, whereas treatment of the chlorodiene with aqueous hydrochloric acid led mainly to 1,4-dichloro-2-methylbut-2-ene.

The trichloropentenes formed, particularly when gaseous chlorine was used, probably came from both substitution in the dichloropentenes and addition to the 2-chloromethylbutadiene. Thus, chlorination of 1,4-dichloro-2-methylbut-2-ene (III) by a solution of chlorine in carbon tetrachloride gave mainly 3,4-dichloro-2-chloromethylbut-1-ene (IV) (presumably by substitution and rearrangement), together with some 1,2,3,4-tetrachloro-2-methylbutane. On the other hand, chlorination of compound (III) with sulphuryl chloride in the presence of benzoyl peroxide led almost completely to the addition product, 1,2,3,4-tetrachloro-2-methylbutane (V), together with some (IV) and a compound (VI) of uncertain structure. Compound (VI) may be 1,1,4-trichloro-2-methylbut-2-ene, since from the products of its ozonolysis, which was extremely slow, were isolated the 2,4-dinitrophenylhydrazones of chloroacetaldehyde and of pyruvaldehyde. When the benzoyl peroxide was replaced by an inhibitor, t-butylcatechol, the compounds (IV) and (VI) were the sole products.





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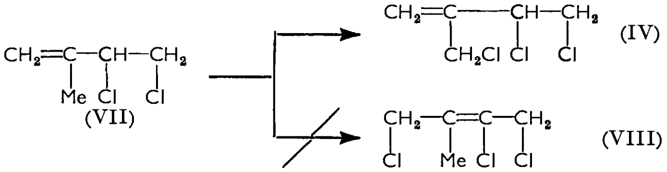
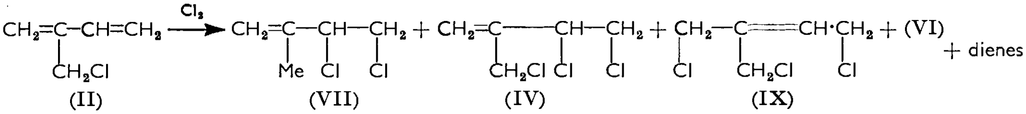
[4] Ultée, *Rec. Trav. chim.*, 1949, **68**, 125.

[5] Bailey, Mainthia, and Abshire, *J. Amer. Chem. Soc.*, 1960, **82**, 6136.

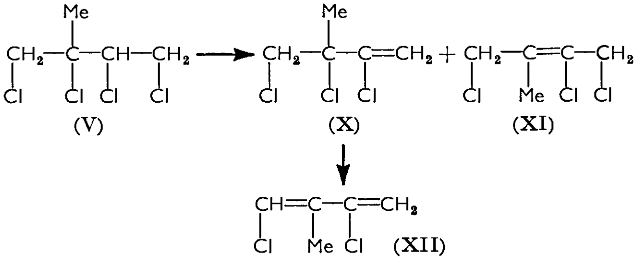
Ultée[4] found that 3,4-dichloro-2-methylbut-1-ene (VII), when treated with sulphuryl chloride in the presence of benzoyl peroxide, also yielded the tetrachloropentane (V), but his statement that the same reaction in the presence of an antioxidant gave 1,3,4-trichloro-2-methylbut-2-ene (VIII) was not confirmed: instead, the major product from the latter reaction was 3,4-dichloro-2-chloromethylbut-1-ene (IV) [with some tetrachloropentane (V)]. Proof of the structure of the product (VIII) depended largely on its conversion into chloroacetic acid on oxidation with potassium permanganate. Although this conversion was confirmed, spectroscopic evidence and the formation of 1,3,4-trichlorobutan-2-one on ozonolysis indicated that structure (IV) was correct.



Chlorination of 2-chloromethylbutadiene, either by chlorine in carbon tetrachloride or by sulphuryl chloride, gave a complex mixture which included unidentified dienes, 3,4-dichloro-2-methylbut-1-ene (VII), 3,4-dichloro-2-chloromethylbut-1-ene (IV), 1,4-dichloro-2-chloromethylbut-2-ene (IX), and the compound (VI). The structure of compound (IX) was assigned on the basis of its ozonolysis to 1,3-dichloroacetone and chloroacetaldehyde. Compound (VII) was an unexpected product, and presumably arose by 1,4-addition of hydrogen chloride (observed as a product of the reaction) to the diene, and allylic rearrangement. The formation of (VII) from (II) by reaction with concentrated hydrochloric acid was noted (see Experimental).



Dehydrochlorination of 1,2,3,4-tetrachloro-2-methylbutane with alcoholic alkali provided 2,3,4-trichloro-3-methylbut-1-ene (X), and not 1,3,4-trichloro-2-methylbut-1-ene as proposed by Ultée, together with a small amount of 1,2,4-trichloro-3-methylbut-2-ene (XI) and a further dehydrochlorination product of (X), presumably 1,3-dichloro-2-methylbutadiene (XII). The structures of compounds (X) and (XI) were based on their products of ozonolysis and, in addition, (X) was found to contain the $CH_2{=}CRR'$ system from its infrared spectrum. The hydrogen atom at position 2(or 3) is that usually lost on dehydrochlorination of a polychlorobutane by alcoholic alkali. Thus 1,2,3,4-tetrachlorobutane, under these conditions, gives a mixture of 2,3,4-trichlorobut-1-ene and 1,2,4-trichlorobut-2-ene,[6] and 1,2,3,3-tetrachlorobutane similarly provides a mixture of 2,3,3-trichlorobut-1-ene and 1,2,3-trichlorobut-2-ene.[7]



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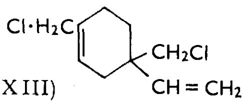
[6] Firestone Rubber and Tire Co., U.S.P. 2,626,964.

[7] Hatch and D'Amico, *J. Amer. Chem. Soc.*, 1951, **73**, 4396.

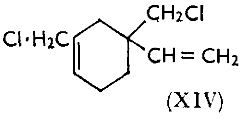
A number of the chloropentenes were found to undergo allylic rearrangement on heating with cuprous chloride. 1,4-Dichloro-2-methylbut-2-ene yielded a mixture of 3,4-dichloro-3-methylbut-1-ene (mainly) and 3,4-dichloro-2-methylbut-1-ene; 3,4-dichloro-2-chloromethylbut-1-ene and 1,4-dichloro-2-chloromethylbut-2-ene were interconvertible; and 2,3,4-trichloro-3-methylbut-1-ene was converted into 1,2,4-trichloro-3-methylbut-2-ene.

$$CH_2{=}C(CH_2Cl){-}CH(Cl){-}CH_2Cl \rightleftharpoons CH_2Cl{-}C(CH_2Cl){=}CH{-}CH_2Cl$$

2-Chloromethylbutadiene dimerised on storage or on heating: spectroscopic study of the dimer indicated that it probably consisted of a mixture of (XIII) and (XIV).



(XIII)



(XIV)

## EXPERIMENTAL

*Chlorination of Isoprene.*—(*a*) *With gaseous chlorine.* (i) Chlorine was passed into a solution of isoprene (100 g.) in chloroform (250 g.), stirred at *ca.* 20°, until there was a weight increase of 104 g. Hydrogen chloride was evolved. Distillation gave fractions: (1) (26·3 g.), b. p. 65°/100 mm. to 92°/50 mm., $n_{\mathrm{D}}^{20}$ 1·4839; (2) (50·2 g.), b. p. 92°/50 mm. to 70°/15 mm., $n_{\mathrm{D}}^{20}$ 1·4951; (3) (20·0 g.), b. p. 70—80°/15 mm., $n_{\mathrm{D}}^{20}$ 1·5019; (4) (12·5 g.), b. p. 80—90°/15 mm., $n_{\mathrm{D}}^{20}$ 1·5090; (5) (17·8 g.), b. p. 90—100°/15 mm., $n_{\mathrm{D}}^{20}$ 1·5180; (6) (53·8 g.), b. p. 100—110°/15 mm., $n_{\mathrm{D}}^{20}$ 1·5221; (7) (11·6 g.), b. p. 110—190°/15 mm., $n_{\mathrm{D}}^{20}$ 1·5340; and residue (19·7 g.). Infrared-spectroscopic examination of these fractions showed, by comparison with the spectra of known compounds (below), that (1) was a mixture of 3,4-dichloro-2- and 3,4-dichloro-3-methylbut-1-ene; (2) a mixture of 1,4-dichloro-2-methylbut-2-ene and the compound of uncertain structure (VI); (3) a mixture of compound (VI) and 3,4-dichloro-2-chloromethylbut-1-ene (IV); (4) was largely (IV); (5) and (6) were mainly 1,4-dichloro-2-chloromethylbut-2-ene (IX); (7) contained 1,2,3,4-tetrachloro-2-methylbutane.

(ii) Reaction as in (i) but with only 85 g. weight increase gave, in addition to unchanged isoprene and the mixture of dichloropentenes as above, a fraction (18·0 g.), b. p. 50—65°/100 mm., $n_{\mathrm{D}}^{20}$ 1·4670, identified as 2-chloromethylbutadiene by comparison with that below.

(*b*) *With a solution of chlorine.* A number of experiments were carried out at temperatures of $-40°$ to 35°, with and without nitrogen passing through the solution to remove hydrogen chloride, but there was little variation in the products.

Isoprene (100 g.) in carbon tetrachloride (100 c.c.) was stirred at *ca.* 20° and a solution of chlorine (107 g.) in carbon tetrachloride (915 c.c.) added during 2 hr. Distillation gave fractions: (1) (13·1 g.), b. p. <50°/100 mm., $n_{\mathrm{D}}^{20}$ 1·4759; (2) (22·9 g.), b. p. 50—70°/100 mm., $n_{\mathrm{D}}^{20}$ 1·4792; (3) (11·0 g.), b. p. 70°/100 mm. to $-65°$/15 mm., $n_{\mathrm{D}}^{20}$ 1·4696; (4) (74·9 g.), b. p. 65—75°/15 mm., $n_{\mathrm{D}}^{20}$ 1·4939; (5) (12·6 g.), b. p. 75—115°/15 mm., $n_{\mathrm{D}}^{20}$ 1·5113; and residue (10·2 g.). Fraction (2) was largely 2-chloromethylbutadiene (77·6% by gas-chromatography), and (4) was mainly 1,4-dichloro-2-methylbut-2-ene (infrared spectrum).

*Chlorination of* 1,4-*Dichloro-2-methylbut-2-ene.*—(*a*) *With a solution of chlorine.* The olefin (14 g.) in carbon tetrachloride (25 c.c.) was treated with a solution of chlorine (7 g.) in carbon tetrachloride (50 c.c.), and the mixture stored for 48 hr. before distillation, which gave fractions: (1) (0·9 g.), b. p. 46—76°/11 mm., $n_{\mathrm{D}}^{20}$ 1·4669; (2) (10·7 g.), b. p. 76—80°/11 mm., $n_{\mathrm{D}}^{20}$ 1·5026; (3) (4·2 g.), b. p. 80—96°/11 mm., $n_{\mathrm{D}}^{20}$ 1·5040; and residue (1·4 g.). Fraction (2) was found by infrared spectroscopy to be a 3 : 2 mixture of 3,4-dichloro-2-chloromethylbut-1-ene (IV) and (VI) (Found: C, 34·85; H, 4·3; Cl, 61·0. Calc. for $C_5H_7Cl_3$: C, 34·6; H, 4·0; Cl, 61·4%). Fraction 3 contained (IV) and 1,2,3,4-tetrachloro-2-methylbutane.

(*b*) *With sulphuryl chloride.* (i) The olefin (100 g.), containing benzoyl peroxide (1·2 g.), was treated with sulphuryl chloride (98 g.) dropwise at 90—100°, then heated for a further hr.

The main product (124 g.), b. p. 97—105°/14 mm., $n_D^{20}$ 1·5060—1·5069 (Found: C, 28·95; H, 3·8; Cl, 65·9. Calc. for $C_5H_8Cl_4$: C, 28·6; H, 3·8; Cl, 67·6%), consisted almost entirely of 1,2,3,4-tetrachloro-2-methylbutane, with <5% of trichlorobutenes.

The combined low-boiling fractions (b. p. <97°/14 mm.) from several experiments were redistilled to provide material, b. p. 70—95°/15 mm., shown spectroscopically to consist of a mixture of (IV) and (VI).

(ii) The olefin (20 g.) was chlorinated with sulphuryl chloride as in (i), except that the benzoyl peroxide was replaced by t-butylcatechol. There were obtained fractions: (1) (10·0 g.), b. p. 69—74°/14 mm., $n_D^{20}$ 1·4978; (2) (5·9 g.), b. p. 74—80°/14 mm., $n_D^{20}$ 1·5038; (3) (5·8 g.), b. p. 80—85°/14 mm., $n_D^{20}$ 1·5047; and residue (1·1 g.). Spectroscopic examination of these fractions showed that fraction (1) consisted largely of (VI); (3) was (IV); and (2) was intermediate in composition.

*Chlorination of* 3,4-*Dichloro*-2-*methylbut*-1-*ene*.—The olefin (50 g.) (prepared by reaction of 1-chloro-3-methylbut-2-ene with sulphuryl chloride in the presence of t-butylcatechol, which was found to be better than quinol [4]), containing t-butylcatechol, was treated with sulphuryl chloride (49 g.), with gentle heating (water-bath) continuing throughout the addition and for a further 2 hr. There were obtained fractions: (1) (5·4 g.), b. p. 42—45°/15 mm., $n_D^{20}$ 1·4625; (2) (2·5 g.), b. p. 45—84°/15 mm., $n_D^{20}$ 1·4810; (3) (34·3 g.), b. p. 84—87°/15 mm., $n_D^{20}$ 1·5072; (4) (3·6 g.), b. p. 87—92°/15 mm., $n_D^{20}$ 1·5085; (5) (9·5 g.), b. p. 92—99°/15 mm., $n_D^{20}$ 1·5070; and residue (1·5 g.). Fractions 1 and 2 consisted of the original olefin and compound (VI); (3) (Found: C, 34·3; H, 4·2; Cl, 61·7. $C_5H_7Cl_3$ requires C, 34·6; H, 4·0; Cl, 61·4%) was 3,4-*dichloro*-2-*chloromethylbut*-1-*ene* (IV); and (5) was the tetrachloropentane (V).

*Chlorination of* 2-*Chloromethylbutadiene*.—(*a*) *With a solution of chlorine*. The diene (77 g.) was treated, with stirring at room temperature, with a solution of chlorine (54 g.) in carbon tetrachloride (500 c.c.). Distillation of the product gave fractions: (1) (24·7 g.), b. p. 62—70°/50 mm., $n_D^{20}$ 1·4728; (2) (5·1 g.), b. p. 44—62°/15 mm., $n_D^{20}$ 1·4930; (3) (6·1 g.), b. p. 62—69°/15 mm., $n_D^{20}$ 1·4973; (4) (10·4 g.), b. p. 69—75°/15 mm., $n_D^{20}$ 1·4961; (5) (7·3 g.), b. p. 75—80°/15 mm., $n_D^{20}$ 1·5018; (6) (10·2 g.), b. p. 80—85°/15 mm., $n_D^{20}$ 1·5080; (7) (5·8 g.), b. p. 85—90°/15 mm., $n_D^{20}$ 1·5110; (8) (4·7 g.), b. p. 90—95°/15 mm., $n_D^{20}$ 1·5141; (9) (30·0 g.), b. p. 95—101°/15 mm., $n_D^{20}$ 1·5211; and residue (6·3 g.). Ultraviolet and infrared spectroscopic examination showed that these fractions contained 3,4-dichloro-2-methylbut-1-ene (fractions 1 and 2), conjugated dienes (fractions 2 and 3), compound (VI) (fractions 4 and 5), 3,4-dichloro-2-chloromethylbut-1-ene (fractions 6—8), and 1,4-dichloro-2-chloromethylbut-2-ene (fraction 9).

(*b*) *With sulphuryl chloride*. Reaction of the diene (40 g.) and sulphuryl chloride (53 g.) gave a product which provided distillation fractions similar in nature to those from (*a*).

*Hydrochlorination of* 2-*Chloromethylbutadiene*.—(*a*) The diene (20 g.), cuprous chloride (10 g.), ammonium chloride (4 g.), and concentrated hydrochloric acid (75 c.c.) were shaken together at room temperature for 17 hr., and the product was extracted with ether and worked up normally to give fractions: (1) (1·4 g.), b. p. 80—85°/50 mm., $n_D^{20}$ 1·4745; (2) (2·7 g.), b. p. 85—90°/50 mm., $n_D^{20}$ 1·4791; (3) (12·9 g.), b. p. 90—93°/50 mm., $n_D^{20}$ 1·4900. Fractions (1) and (2) were shown spectroscopically to be mixtures of 3,4-dichloro-2-methylbut-1-ene and 1,4-dichloro-2-methylbut-2-ene; (3) was mainly the last compound.

(*b*) The diene (20 g.) was cooled in solid carbon dioxide and added slowly to liquid hydrogen chloride at −90°. The mixture was maintained at about this temperature for 6 hr. and then allowed to warm to room temperature. Distillation gave fractions: (1) (13·1 g.), b. p. 55°/50 mm. to 37°/15 mm., $n_D^{20}$ 1·4643; (2) (2·5 g.), b. p. 37—55°/15 mm., $n_D^{20}$ 1·4711; (3) (2·6 g.), b. p. 55—57°/15 mm., $n_D^{20}$ 1·4871. Fraction (1) was 3,4-dichloro-3-methylbut-1-ene, which was also a major component of (2); (3) contained some 1,4-dichloro-2-methylbut-2-ene.

*Dehydrochlorination of* 1,2,3,4-*Tetrachloro*-2-*methylbutane*.—The tetrachloropentane (100 g.) was added slowly at room temperature to a stirred solution of potassium hydroxide (35 g.) in aqueous ethanol: potassium chloride was precipitated. After 1 hour's further stirring water was added and the product extracted with ether. There were obtained fractions: (1) (13·7 g.), b. p. 40—59°/15 mm., $n_D^{20}$ 1·5005; (2) (27·4 g.), b. p. 59—65°/15 mm., $n_D^{20}$ 1·4930; (3) (7·1 g.), b. p. 65—80°/15 mm., $n_D^{20}$ 1·4995; (4) (26·8 g.), b. p. 80—101°/15 mm., $n_D^{20}$ 1·5017; and residue (1·3 g.). Spectroscopically it was found that fraction (1) contained conjugated dienes; (2) was 2,3,4-trichloro-3-methylbut-1-ene; (3) was a mixture; and (4) contained unchanged tetrachloropentane.

The products (fraction 2 and higher) from several runs were combined and fractionated in a

15-in., helices-packed, heated column to provide pure 2,3,4-*trichloro*-3-*methylbut*-1-*ene* (92 g.), b. p. 64—67·5°/15 mm., $n_D^{20}$ 1·4925 (Found: C, 34·3; H, 3·8; Cl, 61·45. $C_5H_7Cl_3$ requires C, 34·6; H, 4·0; Cl, 61·4%), and fractions (43 g.), b. p. 80—96°/15 mm., $n_D^{20}$ 1·5149—1·5051, containing 1,2,4-trichloro-3-methylbut-2-ene. Redistillation of the latter gave 1,2,4-*trichloro*-3-*methylbut*-2-*ene*, b. p. 83—86°/15 mm., $n_D^{20}$ 1·5093 (Found: C, 34·7; H, 4·1; Cl, 59·8%).

Fractionation of the low-boiling, dehydrochlorination product gave material, b. p. 63—66°/50 mm., $n_D^{20}$ 1·5060, with a conjugated diene system (ultraviolet spectrum), and having an infrared spectrum in agreement with the structure 1,3-dichloro-2-methylbutadiene (XII). Dehydrochlorination of 2,3,4-trichloro-3-methylbut-1-ene, as above, yielded the same diene, b. p. 64—70°/50 mm., $n_D^{20}$ 1·5063.

*Isomerisation of Olefins.*—(*a*) 1,4-*Dichloro*-2-*methylbut*-2-*ene*. The olefin (70·9 g.), containing cuprous chloride (1 g.) and copper powder (0·5 g.), was heated at 140—150° (bath) and the crude product (b. p. <80°/50 mm.) taken off overhead from a heated, helices-packed column. Redistillation gave fractions: (1) (23·4 g.), b. p. 58—61°/50 mm., $n_D^{20}$ 1·4651; (2) (11·5 g.), b. p. 61—68°/50 mm., $n_D^{20}$ 1·4670; and residue (6·5 g.). Spectroscopic analysis showed that fraction (1) consisted of 3,4-dichloro-3-methylbut-1-ene, and (2) contained 70% of this and 30% of 3,4-dichloro-2-methylbut-1-ene.

(*b*) 3,4-*Dichloro*-2-*chloromethylbut*-1-*ene*. Olefin (10 g.) and cuprous chloride (0·2 g.) were heated together at *ca.* 200° (bath) for ½ hr., flashed off from the catalyst, and redistilled. In addition to unchanged material there was obtained one fraction (3·5 g.), b. p. 92—98°/15 mm., $n_D^{20}$ 1·5130, which was found spectroscopically to contain 1,4-dichloro-2-chloromethylbut-2-ene (*ca.* 35%).

(*c*) 1,4-*Dichloro*-2-*chloromethylbut*-2-*ene*. Olefin (25 g.) was heated, in the presence of cuprous chloride (0·2 g.), to 110°, and distillate (18·5 g.) with b. p. <80°/15 mm. removed at the head of the column. This distillate was shown by spectroscopic examination to contain *ca.* 85% of 3,4-dichloro-2-chloromethylbut-1-ene.

(*d*) 2,3,4-*Trichloro*-3-*methylbut*-1-*ene*. Olefin (10 g.) was treated as in (*b*). Redistillation gave fractions: (1) (0·6 g.), b. p. 60—80°/13 mm., $n_D^{20}$ 1·5010; and (2) (4·4 g.), b. p. 80—84°/13 mm., $n_D^{20}$ 1·5128. From the spectra of these fractions, (1) was a mixture of starting material and 1,2,4-trichloro-3-methylbut-2-ene, and (2) was entirely the latter compound.

*Structure of the Olefins.*—(*a*) 2-*Chloromethylbutadiene*. A large quantity of this diene was fractionated through a 4-ft., helices-packed, heated column and fractions of b. p. 47·5—53·5°/100 mm., $n_D^{20}$ 1·4800—1·4784 (Found: C, 58·5; H, 7·0; Cl, 34·8. Calc. for $C_5H_7Cl$: C, 58·5; H, 6·8; Cl, 34·6%), appeared to be the middle cut. Only minor differences were evident in the infrared spectra of these fractions.

A sample of the diene was separated by gas-chromatography into 2-chloromethylbutadiene (86·4%) having no infrared absorption due to a methyl group (1379 cm.$^{-1}$), and two other fractions (10% and 3·3%) the larger of which had such a methyl band and may well be 1-chloro-2-methylbutadiene.

The diene (6 g.) was suspended in water (100 c.c.) with vigorous stirring, and an aqueous solution of potassium permanganate in water added gradually, with water-cooling of the mixture, until the total volume was *ca.* 500 c.c. Thereafter solid permanganate was added in small portions up to a total of 53 g. (including that used in solution). The mixture was stored overnight at room temperature, then filtered from manganese dioxide and evaporated to *ca.* 80 c.c. under reduced pressure. Acidification (Congo Red) with hydrochloric acid was followed by ether-extraction. Final distillation provided chloroacetic acid (2·0 g.), b. p. 85—90°/15 mm., which solidified. Crystallisation from light petroleum (b. p. 40—60°) gave this acid with m. p. and mixed m. p. 55—57° (*p*-bromophenacyl ester, m. p. and mixed m. p. 102—104°).

The diene (6 g.) and 1,4-naphthaquinone (3·5 g.) were heated together at 80° for 4 hr.; the mixture soon became blue and after *ca.* 1 hr. was filled with solid. The cooled product was triturated with methanol and filtered to give a blue solid, m. p. 189—191° (from acetone) (Found: C, 67·75; H, 4·6; Cl, 14·7. Calc. for $C_{15}H_{13}ClO_2$: C, 69·1; H, 5·0; Cl, 13·6%). This impure substituted tetrahydroanthraquinone was purified by treatment of an ethanolic solution with charcoal and then had m. p. 144—146° (Found: C, 70·2; H, 4·3; Cl, 13·8%) (lit.,[1] m. p. 146°). Attempts to oxidise this material in slightly alkaline, ethanolic solution with air or oxygen proved troublesome since the alkali was rapidly consumed, and there was finally obtained an impure product which after many recrystallisations from ethanol, benzene–light petroleum, and benzene yielded a small quantity of 2-chloromethylanthraquinone, m. p.

167—168°, undepressed on admixture with authentic 2-chloromethylanthraquinone, but depressed to 140° on admixture with synthetic 1-chloro-2-methylanthraquinone. A more satisfactory method of oxidation, which gave nearly quantitative yields, consisted of treatment with the stoicheiometric amount of chromic oxide in acetic acid at *ca.* 60° (¼ hr.) followed by precipitation with water and recrystallisation of the 2-chloromethylanthraquinone, m. p. 167—169° (from ethyl acetate) (Found: C, 70·0; H, 3·4; Cl, 14·0. Calc. for $C_{15}H_9ClO_2$: C, 70·2; H, 3·6; Cl, 13·85%).

1-Chloro-2-methylanthraquinone was synthesised from 2-methylanthraquinone by the method of Dickey *et al.*[8] Several recrystallisations, finally from ethyl acetate, gave material with m. p. 175—178° (Found: C, 69·75; H, 3·7; Cl, 14·2. Calc. for $C_{15}H_9ClO_2$: C, 70·2; H, 3·5; Cl, 13·85%). 2-Chloromethylanthraquinone was also synthesised from 2-methylanthraquinone both by the method of Bhavsar *et al.*[9] and that of Conant and Fieser;[10] final recrystallisation from benzene yielded material of m. p. 166—167° (Found: C, 70·1; H, 3·65; Cl, 13·95%).

The 2-chloromethylbutadiene on prolonged storage or on heating, followed by redistillation, gave fractions of *dimer*, b. p. 133—138°/15 mm., $n_D^{20}$ 1·5254—1·5264 (Found: C, 58·4; H, 6·9; Cl, 34·5, 34·6. $C_{10}H_{14}Cl_2$ requires C, 58·5; H, 6·8; Cl, 34·6%). The infrared spectra of the fractions showed the presence of displaced vinyl groups, and were not in disagreement with the structures (XIII) and (XIV).

(*b*) 3,4-*Dichloro*-2-*methylbut*-1-*ene*. This was prepared by reaction of sulphuryl chloride with 1-chloro-3-methylbut-2-ene (Ultée's method,[4] except that better yields were obtained when quinol was replaced by the more oil-soluble t-butylcatechol). It had b. p. 58—63°/40—45 mm., $n_D^{20}$ 1·4695—1·4701 (Found: C, 43·1; H, 5·8; Cl, 50·75. Calc. for $C_5H_8Cl_2$: C, 43·2; H, 5·75; Cl, 51·1%), and its infrared spectrum was in agreement with the stated structure.

The olefin (10 g.) in ethyl acetate (25 c.c.) was treated with ozonised oxygen for *ca.* 24 hr. at room temperature; the ozonide was decomposed with boiling water and the mixture extracted with ether. The aqueous layer provided formaldehyde 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 152—154°. The organic phase (7·0 g.), after removal of the ether, was found spectroscopically to contain *ca.* 80% of unchanged olefin: concentration of the non-olefinic constituent by distillation gave material which provided the 2,4-*dinitrophenylhydrazone*, m. p. 109—110° (Found: C, 37·45; H, 3·2; Cl, 21·5; N, 17·5. $C_{10}H_{10}Cl_2N_4O_4$ requires C, 37·4; H, 3·1; Cl, 22·1; N, 17·45%), and *semicarbazone* (prepared without the use of sodium acetate), m. p. 116—118° (Found: C, 30·75; H, 4·6; Cl, 34·4; N, 21·3. $C_5H_9Cl_2N_3O$ requires C, 30·3; H, 4·55; Cl, 35·8; N, 21·2%), of 3,4-dichlorobutan-2-one. No depression was given on admixture of the above derivatives with those (m. p. 109—110° and 117—118°, respectively) from synthetic 3,4-dichlorobutan-2-one (b. p. 55—56°/15 mm.) obtained by chlorination (chlorine in carbon tetrachloride) of methyl vinyl ketone at 0° (cf. Naftali[11]).

(*c*) 3,4-*Dichloro*-3-*methylbut*-1-*ene*. This was obtained by: (i) fractionation of the material, boiling between 2-chloromethylbutadiene and 1,4-dichloro-2-methylbut-2-ene, from the chlorination of isoprene; (ii) isomerisation of 1,4-dichloro-2-methylbut-2-ene with cuprous chloride; and (iii) hydrochlorination of 2-chloromethylbutadiene. Refractionated material had b. p. 60—63°/50 mm., $n_D^{20}$ 1·4652 (Found: C, 43·0; H, 5·6; Cl, 50·6%). Ozonolysis of the olefin as above gave back much unchanged material. From the aqueous phase formaldehyde 2,4-dinitrophenylhydrazone was again isolated, and the organic phase provided a 2,4-*dinitrophenylhydrazone*, m. p. 120—122° (from methanol) (Found: C, 43·3; H, 4·6; Cl, 10·6; N, 17·0. $C_{12}H_{15}ClN_4O_5$ requires C, 43·6; H, 4·55; Cl, 10·7; N, 16·95%), prepared in ethanol solution, of what was evidently a chloroethoxyisobutyraldehyde.

Further ozonolysis of olefin (3·4 g.), for 40 hr., gave an aldehyde (1·7 g.) which was oxidised with aqueous potassium permanganate (2 g.) at room temperature. The manganese dioxide was filtered off, the solution was extracted with ether, and the acid products were removed by shaking the ethereal extract with sodium hydrogen carbonate solution. The acid (0·7 g.) finally isolated had a spectrum identical with that of synthetic αβ-dichloroisobutyric acid (obtained by chlorination of methacrylic acid), b. p. 109—112°/15 mm., $n_D^{20}$ 1·4680; and the

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[8] Dickey, Towne, Bloom, Taylor, Wallace, Sagal, McCall, and Hedberg, *Ind. Eng. Chem.*, 1956, **48**, 209.

[9] Bhavsar, Tilak, and Venkataraman, *J. Sci. Ind. Res., India*, 1957, **16**, *B*, 392.

[10] Conant and Fieser, *J. Amer. Chem. Soc.*, 1924, **46**, 1858.

[11] Naftali. *Bull. Soc. chim. France.* 1937. **4**. 340.

p-*bromophenacyl esters*, m. p. 80—82° (Found: C, 40·4; H, 3·1; Br, 22·6; Cl, 19·8. $C_{12}H_{11}BrCl_2O_3$ requires C, 40·7; H, 3·1; Br, 22·6; Cl, 20·1%), were identical.

(*d*) 1,4-*Dichloro*-2-*methylbut*-2-*ene*. Fractionation of the olefin, obtained from the chlorination of isoprene, through a 4-ft., helices-packed column gave fractions, b. p. 93—97·0°/50 mm., $n_D^{20}$ 1·4925—1·4934 (Found: C, 42·8; H, 5·65; Cl, 50·7%), probably containing variable proportions of *cis-trans*-isomers.

Ozonolysis as above afforded, from the aqueous phase, chloroacetaldehyde 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 158—160° (Found: C, 37·3; H, 2·7; Cl, 13·3; N, 21·65. Calc. for $C_8H_7ClN_4O_4$: C, 37·15; H, 2·7; Cl, 13·7; N, 21·7%), and from the organic phase fractions yielding the above derivative and chloroacetone 2,4-dinitrophenylhydrazone, m. p. 124—125° (Found: C, 39·7; H, 3·45; Cl, 12·9; N, 20·3. Calc. for $C_9H_9ClN_4O_4$: C, 39·6; H, 3·3; Cl, 13·0; N, 20·6%).

(*e*) 3,4-*Dichloro*-2-*chloromethylbut*-1-*ene*. The olefin (10 g.) in ethyl acetate (25 c.c.) was ozonised for 64 hr., and the product worked up as before. The aqueous phase again provided formaldehyde 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 160—162°. The organic phase consisted mainly of unchanged olefin, but from four similar ozonolyses a fraction (3·2 g.), b. p. 89—93°/15 mm., $n_D^{20}$ 1·5023, was obtained which was shown spectroscopically to contain *ca*. 50% of olefin and *ca*. 25% of a chlorinated ketone. It yielded the 2,4-*dinitrophenylhydrazone* (from methanol), m. p. 106—108° (Found: C, 33·4; H, 2·4; Cl, 29·45; N, 15·7. $C_{10}H_9Cl_3N_4O_4$ requires C, 33·75; H, 2·5; Cl, 29·95; N, 15·75%), and *semicarbazone* (from benzene), m. p. 109—110° (Found: C, 26·1; H, 3·4; Cl, 45·6; N, 18·3. $C_5H_8Cl_3N_3O$ requires C, 25·8; H, 3·45; Cl, 45·8; N, 18·1%), of 1,3,4-trichlorobutan-2-one, identical with the derivatives of the authentic ketone, b. p. 89—91°/15 mm., $n_D^{20}$ 1·4969, prepared by chlorination of chloromethyl vinyl ketone at −10° in carbon tetrachloride (cf. Catch *et al*.[12]). The chloromethyl vinyl ketone was obtained by dehydrochlorination of 1,4-dichlorobutan-2-one, itself synthesised by the reaction of chloroacetyl chloride with ethylene in the presence of aluminium chloride.[12,13]

(*f*) 2,3,4-*Trichloro*-3-*methylbut*-1-*ene*. The olefin (9 g.), in ethyl acetate, was ozonised for 22 hr. and worked up as before. The aqueous phase provided formaldehyde 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 162—164°. The organic phase on distillation gave unchanged olefin (4·1 g.) and a fraction (3·0 g.), b. p. 110—112°/15 mm., consisting largely of αβ-dichloroisobutyric acid (infrared spectrum), which provided the *p*-bromophenacyl ester, m. p. and mixed m. p. 80—82°, as above.

(*g*) 1,4-*Dichloro*-2-*chloromethylbut*-2-*ene*. Redistillation of the olefin, obtained from chlorination of 2-chloromethylbutadiene (above), gave pure 1,4-*dichloro*-2-*chloromethylbut*-2-*ene*, b. p. 96—97·5°/15 mm., $n_D^{20}$ 1·5215 (Found: Cl, 61·4. $C_5H_7Cl_3$ requires Cl, 61·4%).

This olefin (10 g.) was ozonised as above for 24 hr. The product, on distillation, gave fractions: (1) (2·7 g.), b. p. 65—84°/15 mm., and (2) (6·2 g.), b. p. 84—98°/15 mm., $n_D^{20}$ 1·5120. A cooled methanolic solution of fraction (1) yielded 1,3-dichloroacetone, m. p. 42—44° (identified spectroscopically) [2,4-dinitrophenylhydrazone, m. p. 131—132·5° (lit.,[14] 132—133°) (Found: C, 35·35; H, 2·7; Cl, 22·85; N, 18·25. Calc. for $C_9H_8Cl_2N_4O_4$: C, 35·2; H, 2·6; Cl, 23·1; N, 18·25%]. Fraction (2) was largely unchanged olefin, but from it was extracted a small quantity of acid, identified as chloroacetic acid from its infrared spectrum.

(*h*) 1,2,4-*Trichloro*-3-*methylbut*-2-*ene*. The olefin (10 g.) was ozonised in the normal way. The aqueous phase provided chloroacetone 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 124·5—126°. The organic phase on distillation gave fractions (1·7 g.) from which the same derivative was obtained, and fractions (7·0 g.), b. p. 72—85°/12 mm., which consisted mainly of unchanged olefin but from which was extracted chloroacetic acid (*p*-bromophenacyl ester, m. p. and mixed m. p. 104—105°).

(*i*) *Compound* (VI). Redistillation of this material, from the chlorination of 1,4-dichloro-2-methylbut-2-ene, gave a fraction, b. p. 71—75°/12 mm., $n_D^{20}$ 1·4991 (Found: C, 35·8; H, 4·2; Cl, 59·7. Calc. for $C_5H_7Cl_3$: C, 34·6; H, 4·0; Cl, 61·4%), probably containing some unchanged dichloropentene; and a fraction, b. p. 75—80°/12 mm., $n_D^{20}$ 1·5023 (Found: C, 34·4; H, 4·25; Cl, 60·5%), found spectroscopically to contain some 3,4-dichloro-2-chloromethylbut-1-ene.

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[12] Catch, Elliott, Hey, and Jones, *J*., 1948, 278.

[13] Arbuzov and Dyatkin, *Doklady Akad. Nauk S.S.S.R.*, 1956, **111**, 1249.

[14] Johnson, *J. Amer. Chem. Soc.*, 1953, **75**, 2720.

No pure sample of compound (VI) free from other chlorinated pentenes could be obtained, but ozonolysis of the lower-boiling fraction yielded material from which the 2,4-dinitrophenylhydrazones of chloroacetaldehyde (m. p. and mixed m. p. 158—160°) and pyruvaldehyde [m. p. and mixed m. p. 296—297° (decomp.)] (from nitrobenzene) were obtained.

1,4-*Dichlorobutan*-2-*one*.—This was prepared (in poor yield) by reaction of chloroacetyl chloride with ethylene in the presence of aluminium chloride.[13] The ketone, b. p. 88—92°/15 mm., $n_D^{20}$ 1·4790, provided a 2,4-*dinitrophenylhydrazone*, m. p. 113—115° (from benzene) (Found: C, 37·45; H, 3·1; Cl, 21·6; N, 17·3. $C_{10}H_{10}Cl_2N_4O_4$ requires C, 37·4; H, 3·1; Cl, 22·1; N, 17·4%), and a *semicarbazone* (prepared without the use of sodium acetate), m. p. 97—98° (decomp.) (Found: C, 30·45; H, 4·7; Cl, 35·5; N, 21·1. $C_5H_9Cl_2N_3O$ requires C, 30·3; H, 4·55; Cl, 35·8; N, 21·2%).

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