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735. *Trihalogenomethyl Compounds of Potential Therapeutic Interest. Part V.*[1] *The Reaction of Chloral with Diazomethane.**

By R. E. Bowman, A. Campbell, and W. R. N. Williamson.

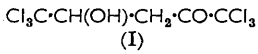
The reaction of two moles of chloral with one of diazomethane in diethyl ether has been shown to give 1,1,1,5,5,5-hexachloro-3,4-epoxypentan-2-ol (II), with the configuration (VI).

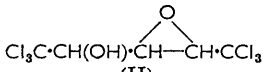
Schlotterbeck [2] reported that reaction of diazomethane with an excess of chloral yielded an oil, $C_3H_3Cl_3O$, later shown [3] to be 3,3,3-trichloro-1,2-epoxypropane, and a crystalline solid (A), $C_5H_4Cl_6O_2$, m. p. 88°, formulated as 1,1,1,5,5,5-hexachloro-4-hydroxypentan-2-one (I).

In our hands, the major product was a new isomeric material (B), m. p. 85—86°, accompanied by a small quantity of a mixture of (A) and (B), not separable by crystallisation.

The infrared spectrum of (B) showed the presence of hydroxyl (3400) and epoxide CH (3030 cm.$^{-1}$) but no methylene or carbonyl absorption. The nuclear magnetic resonance (n.m.r.) spectrum showed the presence of four protons, two as doublets at 5·47 (J = 1·95 c./sec.) and 5·84 τ (J = 1·65 c./sec.), the third a triplet at 6·06 τ (J_1 = 1·95; J_2 = 1·65 c./sec.), and the fourth a singlet at 6·16 τ. The structure of B must therefore be (II); degradative and synthetical evidence will be presented to show that this structure is correct.

The pentanol (II) gave a monomethyl ether, a monoacetate and a monobenzoate; the secondary nature of the hydroxyl grouping was demonstrated by oxidation with chromium trioxide to a crystalline ketone [$\nu_{max.}$ 3032, 3008 (epoxide CH), 1768 cm.$^{-1}$


(I)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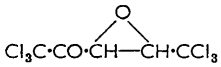
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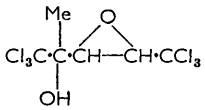
(IV)

($Cl_3C{\cdot}CO$)], which could be reduced with lithium or sodium borohydride to a mixture of the original pentanol (II) and a higher-melting epimer. Oxidation of the epimer gave the ketone (III).

Reaction of the ketone (III) with methylmagnesium iodide gave a poor yield of the tertiary alcohol (IV). Reductive dehalogenation of the ketone (III) over 5% palladium–charcoal and potassium carbonate produced an oil which, with the same Grignard reagent, yielded crude 2-methylpentane-2,3-diol, characterised as its di-*p*-nitrobenzoate.

Reductive dehalogenation of the pentanol (II) yielded *erythro*-pentane-2,3-diol isolated as its di-*p*-nitrobenzoate and bis-3,5-dinitrobenzoate.[4] The diol was further characterised by periodate oxidation to give acetaldehyde and propionaldehyde. The products of reductive dehalogenation of the pentanol (II) and the ketone (III) indicate that chlorine is removed before attack on the epoxides takes place since the epoxide C–O bond cleaved must be the least deactivated one [5] and hence adjacent to the newly formed methyl group.

* A short summary of this work was read at the XIXth Congress of Pure and Applied Chemistry, London, 1963.

[1] Part IV, Bowman, Closier, and Islip, preceding Paper.
[2] Schlotterbeck, *Ber.*, 1909, **42**, 2559.
[3] Arndt and Eistert, *Ber.*, 1928, **61**, 1118.
[4] Lucas, Schlatter, and Jones, *J. Amer. Chem. Soc.*, 1941, **63**, 22.
[5] Parker and Isaacs, *Chem. Rev.*, 1959, **59**, 746.

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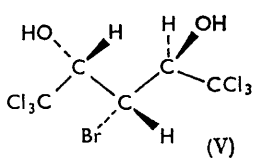
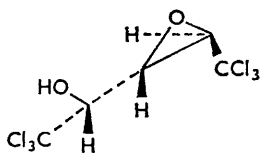
The solution from catalytic reduction of the pentanol (II) gave pentane-2,3-dione bis-2,4-dinitrophenylhydrazone, m. p. 235—237°. The authentic compound, prepared from 4-hydroxypentan-3-one, had m. p. 271—272°, but the infrared spectra, determined in chloroform solution, of the two materials were virtually identical, so the first compound was a dimorphic form of the second and was presumably produced by catalytic oxidation of pentane-2,3-diol, probably to a mixture of the corresponding hydroxy-ketones and dione during filtration of the catalyst. The isolation of acetaldehyde 2,4-dinitrophenylhydrazone in the same reaction sequence can be attributed to the same type of oxidation (of the solvent).

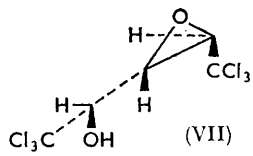
The pentanol (II), when refluxed with 60% hydrobromic acid–acetic acid, gave 3-bromo-1,1,1,5,5,5-hexachloropentane-2,4-diol (V), presumably mixed with some of the triol (VIII) since the initial product consumed some sodium metaperiodate, and this treatment effected a purification of the compound. The stability of the bromo-diol to periodate eliminates the possible alternative 2,3-diol structure. Reductive dehalogenation of the bromo-diol gave an impure sample of racemic pentane-2,4-diol, which had infrared peaks at 805 and 842 cm.$^{-1}$, reported for this compound [6] and absent from the *meso*-isomer. The pure diacetate had a retention time of 6·08 min. during gas chromatography at 140° on a 50-m. Golay column coated with polypropene, whilst a (1 : 1·2) mixture of the diacetates of racemic and *meso*-pentane-2,4-diols (the diols were prepared by hydrogenation of acetylacetone over Raney nickel [7]) had retention times of 6·08 and 7·24, minutes, respectively, in the same system. The orders of retention times are assigned from the published values [7] in a similar chromatographic system. No evidence of the presence of any *meso*-diacetate was found in the first chromatogram. Hence the diacetate obtained from the reduction product of the bromo-diol (V) is that of racemic pentane-2,4-diol. In agreement with this, the di-*p*-nitrobenzoate from the reduction diol had a lower melting point than that of the di-*p*-nitrobenzoate of *meso*-pentane-2,4-diol, prepared from the cyclic borate [8] of the diol. Combining the stereochemical results indicated by the isolation of *erythro*-pentane-2,3-diol and racemic pentane-2,4-diol from the pentanol (II), we can write the configuration shown



(V)



(VI)



(VII)

$Cl_3C\cdot[CH\cdot OH]_3\cdot CCl_3$

(VIII)

in structure (VI) for the compound; the configuration (VII) follows for its epimer, and a *trans*-epoxide structure for the ketone (III). The assignment of a *trans*-epoxide configuration agrees with the n.m.r. coupling constant of 1·95 for the epoxide protons.[9] Since the bromo-diol (V) could be reconverted, in good yield, into the pentanol (II) by refluxing with potassium acetate in acetone,[10] the configuration (V) is assigned to it, assuming inversion at C-3 during epoxide formation by a basic reagent.[11]

Acetic acid–concentrated hydrochloric acid-hydrolysis of the pentanol (II), or of its acetate, gave the triol (VIII), characterised as its triacetate and monoacetate. The latter was also obtained by heating the pentanol (II) with hydrogen bromide in acetic acid. The acetyl group is probably on the central oxygen atom, owing to attack on the epoxide

[6] Nagai, Kuribayashi, Shiraki, and Ukita, *J. Polymer Sci.*, 1959, **35**, 295.
[7] Pritchard and Vollmer, *J. Org. Chem.*, 1963, **28**, 1545.
[8] Dale, *J.*, 1961, 916.
[9] Tung, Speziale, and Frazier, *J. Org. Chem.*, 1963, **28**, 1514.
[10] Julian, Cole, Meyer, and Regan, *J. Amer. Chem. Soc.*, 1955, **77**, 4603.
[11] Winstein and Henderson in "Heterocyclic Compounds," ed. Elderfield, John Wiley and Sons, New York, 1950, Vol. I, p. 11.

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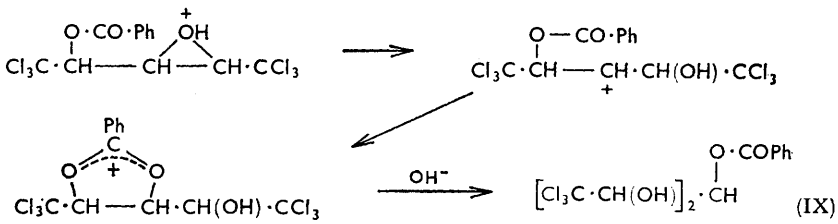
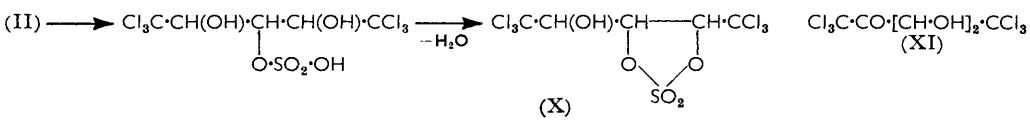
carbon remote from the deactivating trichloromethyl group.[5] The infrared spectrum shows acetyl carbonyl absorption at 1754 cm.$^{-1}$ ($CHCl_3$); acetates of secondary 1,1,1-trichloromethyl alcohols absorb at *ca.* 1768 cm.$^{-1}$ in Nujol.[12] The triol (VIII) consumed two equivalents of sodium metaperiodate and gave one equivalent of formic acid, and reductive dechlorination and reaction of the product with *p*-nitrobenzoyl chloride gave a compound with the correct analysis for pentane-2,3,4-triol tri-*p*-nitrobenzoate. In the acid hydrolysis of the pentanol (II) to the triol, some of the former was recovered unchanged, indicating resistance of the epoxide to hydrolysis; this behaviour is expected of an epoxide flanked by electron-withdrawing groups.[5] On the other hand, acid hydrolysis of the pentanol (II) benzoate gave a monobenzoate which failed to consume periodate and must have the structure (IX). The proposed reaction mechanism is as follows (cf. ref. 13):



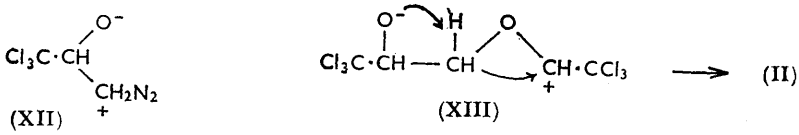
A similar reaction in the sugar series has recently been discussed by Buchanan and Schwarz.[14]

Treatment of the pentanol (II) with concentrated sulphuric acid gave the 5-membered-ring sulphate (X), presumably formed by means of the mechanism shown:



The n.m.r. spectrum was consistent with this structure and eliminated the alternative possibility of a six-membered ring. The infrared absorption (1775s cm.$^{-1}$) in Nujol of the sulphate monoacetate was in agreement, whilst a crude ketone, obtained by chromium trioxide oxidation of the sulphate (X) showed infrared absorption expected of a 1,1,1-trichloromethyl ketone. In contrast with this result the ketone (III), in the presence of its hydrate, reacted very slowly with concentrated sulphuric acid to give 1,1,1,5,5,5-hexachloro-3,4-dihydroxypentan-2-one (XI), which reacted with two equivalents of sodium metaperiodate to yield one equivalent of acid.

It is generally accepted that the reaction of aldehydes with diazomethane involves an intermediate of type (XII).[15] When an excess of chloral is present it could react with the complex to give the intermediate (XIII) which then collapses by the process shown to



give the pentanol (II). An alternative mechanism for the formation of the pentanol (II) is as shown. Rearrangement of the intermediate (XIV) could be responsible for the formation of the ketol (I), and the formation of this compound in low yield may reflect the small amount of rearrangement of the complex (XII) that occurs.

[12] Bowman, White, and Williamson, *J.*, 1964, 1086.
[13] Nayler, *Chem. and Ind.*, 1958, 863, and refs. therein.
[14] Buchanan and Schwarz, *J.*, 1962, 4770.
[15] Gutsche, *Org. Reactions*, 1954, **8**, 364; Eistert (translated and revised by Spangler) in "Newer Methods of Preparative Organic Chemistry," 1st edn., Interscience, New York, 1948, p. 521.

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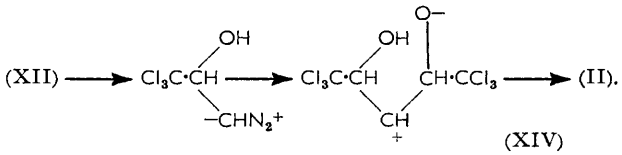
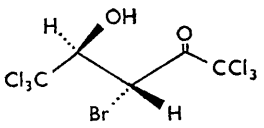
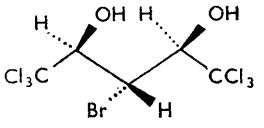


The synthesis of the pentanol (II) was accomplished as follows. 1,1,1,5,5,5-Hexachloro-4-hydroxypentan-2-one [12] heated with bromine, gave 1,1,1,5,5,5-hexachloro-3-bromo-4-hydroxypentan-2-one (XV) which yielded 1,1,1,5,5,5-hexachloro-3-bromopentane-2,4-diol (XVI) on reduction with potassium borohydride. The bromo-diol (XVI) then gave, in poor yield, the epimer (VII) of the pentanol (II) by refluxing with potassium acetate in acetone.[10] A small amount of the epimer was also obtained when the bromoketol (XV) was reduced with aluminium isopropoxide. As the epimer had been converted into the pentanol (II) *via* the ketone (III) this constituted a synthesis of the pentanol (II). The stereochemistry shown in structures (XV) and (XVI) is assigned because of the formation of the epimer from the latter, assuming inversion at C-3 during epoxide formation.

Some alternative routes to the pentanol (II) were investigated. It was hoped to prepare the compound by epoxidation of 1,1,1,5,5,5-hexachloropent-3-en-2-ol (XVII) which was obtained impure by reduction of 1,1,1,5,5,5-hexachloropent-3-en-2-one. However the pentenol (XVII) failed to react with monoperphthalic acid. To obtain information regarding the behaviour of the $Cl_3C{\cdot}CH{=}CH{\cdot}$ system with epoxidising agents,



(XV)



(XVI)

the model compound 5,5,5-trichloropent-3-en-2-ol (XVIII) was prepared. It failed to react with monoperphthalic acid and trifluoroperacetic acid,[16] its acetate did not react with *N*-bromosuccinimide [17] in water–acetic acid, whilst the corresponding ketone, 5,5,5-trichloropent-3-en-2-one, was unchanged by t-butyl hydroperoxide and trifluoroperacetic acid. Reaction of chloral with 3,3,3-trichloro-1-diazopentan-2-one [18] might be expected to give the ketone (III) but did not do so.

(XVII) $R{\cdot}CCl_3$ [R = $Cl_3C{\cdot}CH{=}CH{\cdot}CH(OH)$] RMe (XVIII)

Experimental

1,1,1,5,5,5-*Hexachloro*-3,4-*epoxypentan*-2-*ol* (II).—Chloral (70 g.) in ether (200 ml.) was added gradually to diazomethane [from *N*-nitrosomethylurea (40 g.)] in ether (400 ml.) at 0°. A steady evolution of nitrogen was observed when more than one half of the chloral had been added. When the evolution had ceased and the mixture was colourless the ether was distilled at atmospheric pressure and the residue heated to 130° at 20 mm. to remove 3,3,3-trichloro-1,2-epoxypropane and unreacted chloral. The dark brown or yellow residue gave the *pentanol* (40 g., 54·5%) as colourless prisms, m. p. 85—86° [from light petroleum (b. p. 40—60°)], pK_a (50% EtOH) 12·1 [Found: C, 19·7; H, 1·2; Cl, 69·5; active H, 0·35%; *M* (Rast), 343. $C_5H_4Cl_6O_2$ requires C, 19·5; H, 1·3; Cl, 68·9; active H, 0·31%; *M*, 309]. The compound dissolved in 2N-sodium hydroxide and deposited a solid, presumably a sodium salt, almost immediately, which on trituration with N-hydrochloric acid yielded the starting material (64% recovery). Treatment with acetic anhydride at 100° gave the *acetate*, platelets, m. p. 61—62° (from aqueous methanol) (Found: C, 24·2; H, 2·0. $C_7H_6Cl_6O_3$ requires C, 24·0; H, 1·8%),

[16] Emmons and Pagano, *J. Amer. Chem. Soc.*, 1955, **77**, 89.
[17] Raphael, *J.*, 1949, S 44; 1952, 401.
[18] Brown and Musgrave, *J.*, 1953, 2087; Vardar and Tüccarbasi, *Istanbul Univ. Fak. Mecmusai*, 1953, **18***A*, 423.

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$\nu_{max.}$ (Nujol) 1768 cm.$^{-1}$ (CO). The *benzoate* was obtained as colourless prisms, m. p. 92—93° [from light petroleum (b. p. 40—60°)] (Found: C, 34·9; H, 2·2. $C_{12}H_8Cl_6O_3$ requires C, 34·9; H, 1·9%), $\nu_{max.}$ (Nujol) 1740 cm.$^{-1}$ (CO). Refluxing the pentanol (II) in acetone with anhydrous potassium acetate and methyl iodide for 9 hr. and repetition (2 × 18 hr.) of the process gave the *methyl ether* as a colourless oil, n_D^{22} 1·5046 (Found: C, 22·5; H, 1·8; Cl, 65·9, OMe, 3·7. $C_6H_6Cl_6O_2$ requires C, 22·3; H, 1·9; Cl, 65·9, OMe, 9·6%).

The pentanol (II) did not react with boron trifluoride etherate in benzene,[19] thiourea in methanol,[20] or 1% sulphuric acid in ethanol.

Mixture of Ketol (I) *and Pentanol* (II).—The collected crystallisation residues of the pentanol (II) preparations (from 648 g. chloral), which consisted of a crystalline solid and a gum, were triturated with light petroleum (b. p. 40—60°; 100 ml.) to give a solid (10·1 g.) m. p. 64—74°. Crystallisation from light petroleum (b. p. 60—80°; 50 ml.) gave the mixture as flat microneedles (8·0 g.), m. p. 65°, $\nu_{max.}$ (CCl_4) 3555 (OH) and 1754 cm.$^{-1}$ (CO) (Found: C, 20·0; H, 1·6, $C_5H_4Cl_6O_2$ requires C, 19·5; H, 1·2%). Mixed m. p. with the pentanol (II), 62—64°, and with the ketol (I), 55—64°. The filtrate from the trituration was evaporated and the residue distilled to give an oil (39·9 g.) b. p. 117—119°/0·9 mm. (Found: C, 19·95; H, 1·4%) which crystallised. Repeated crystallisation from light petroleum (b. p. 60—80°) gave the mixture (9·7 g.) as needles, m. p. 57—60° (Found: C, 19·6; H, 1·15%), presumably containing slightly different proportions of the two components. The infrared spectrum of the material (in CCl_4) was essentially the same as that of the previous sample.

A mixture (12·4 g.) of the two samples of the mixture in tetrahydrofuran (50 ml.) was treated dropwise over 10 min. at 10—15° with a solution (37·8 ml.) in tetrahydrofuran of lithium borohydride [21] (0·04 mole). After stirring for a further 10 min. at 15° the solution was poured into ice and 2N-sulphuric acid (100 ml.), and extracted with ether. After washing with sodium hydrogen carbonate solution and water, the dried ($MgSO_4$) extract was evaporated to leave a gum which crystallised as elongated microplates (6·0 g.), m. p. 110—118°. Further crystallisation from benzene–light petroleum (b. p. 60—80°) gave the higher-melting form of 1,1,1,5,5,5-*hexachloropentane*-2,4-*diol*, m. p. 130—132·5° (Found: C, 19·7; H, 2·0. $C_5H_6Cl_6O_2$ requires C, 19·3; H, 1·9%), its infrared spectrum was virtually identical with that of the authentic sample described below. The filtrate from the crystallisation of this compound gave the pentanol (II), m. p. 76—78°, undepressed on admixture with authentic material. A complete separation of the higher- from the lower-melting form had probably not been effected since, on reductive dehalogenation of the diol, the pentane-2,4-diol isolated gave a *di*-p-*nitrobenzoate*, needles, m. p. 142—145° (Found: C, 56·65; H, 4·6; N, 6·35. $C_{19}H_{18}N_2O_8$ requires C, 56·7; H, 4·5; N, 7·0%) which is intermediate between the m. p.s found for the di-*p*-nitrobenzoates of *meso* and racemic pentane-2,4-diols (see below).

1,1,1,5,5,5-*Hexachloropentane*-2,4-*diol*.—1,1,1,5,5,5-Hexachloro-4-hydroxypentan-2-one [12] (15·45 g.) in tetrahydrofuran (55 ml.) was reduced with lithium borohydide (0·05 mole) in tetrahydrofuran (47·2 ml.) at 10° for 25 min. and processed as described above to give an oil which crystallised in the presence of light petroleum (b. p. 40—60°) to give solid (A) (5·6 g.), m. p. 104—115°. Crystallisation of (A) from light petroleum gave the lower-melting *isomer* of the *diol* (4·64 g.), m. p. 105—106° (clears 118—120°) [Found (on sample dried at 57°/1 mm.) C, 19·7; H, 1·9%]. The filtrate from the solid (A) yielded, on evaporation, a further solid (9 g.), m. p. 95—100°, which, by fractional crystallisation from light petroleum (b. p. 60—80°) yielded a further quantity (5·89 g.) of the lower-melting isomer together with the higher-melting *isomer* (1·94 g.), m. p. 120—124° (clears 126—127°) [Found (on sample dried as before): C, 19·5; H, 1·85%]. The m. p.s of these materials indicated that each was probably contaminated with some of the other.

1,1,1,5,5,5-*Hexachloro*-3,4-*epoxypentan*-2-*one* (III).—The pentanol (II) (24 g.), in glacial acetic acid (200 ml.) and concentrated sulphuric acid (5 ml.) was stirred and chromium trioxide (16 g.) was added portionwise at 36—40°. After the addition was complete, the cooling bath was removed and the mixture stirred until the temperature reached 25° (0·5 hr.). Water (300 ml.) was added, the mixture stirred for a few minutes, and extracted with light petroleum (b. p. 40—60°; 5 × 100 ml.) then ether. The extracts were combined and washed with water, sodium hydrogen carbonate solution, and water, dried, ($MgSO_4$), and the solvent was distilled.

[19] Henbest and Wrigley, *J.*, 1957, 4596.
[20] Hall, Hough, and Pritchard, *J.*, 1961, 1537.
[21] Paul and Joseph, *Bull. Soc. chim. France*, 1953, **20**, 758.

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The resulting oil crystallised from light petroleum (b. p. 40—60°) to give the *ketone* (18·15 g.) as plates, m. p. 77—79° (Found: C, 20·0; H, 0·4; Cl, 69·3. $C_5H_2Cl_6O_2$ requires C, 19·6; H, 0·7; Cl, 69·3%), $\nu_{max.}$ (CCl_4) 3032, 3008 (epoxide CH), and 1768 cm.$^{-1}$ (CO). In one large-scale oxidation of the pentanol (II) (106 g.) a mixture (90·3 g.), m. p. 73—75°, of approximately equal quantities of the ketone and its hydrate was isolated. Crystallisation of the mixture from light petroleum (b. p. 60—80°) gave the ketone, and the *hydrate* (mixed with some ketone) as needles, m. p. 75—77° (Found: C, 18·8; H, 1·4; $C_5H_2Cl_6O_2,H_2O$ requires C, 18·5; H, 1·2%), $\nu_{max.}$ 3525 (OH) and 1763 cm.$^{-1}$ (CO). The hydrate–ketone mixture was converted into the ketone by refluxing in benzene to remove the water.

Pentanol (II) *Epimer* (VII).—The ketone (III) (3·07 g.) in tetrahydrofuran (10 ml.) was reduced with 0·0025M-lithium borohydride in tetrahydrofuran (2·3 ml.) at 45° for 10 min. Processing as before gave a solid (0·38 g.), m. p. 152—153° [from light petroleum (b. p. 60—80°)]. Four crystallisations of the solid (0·15 g.) from light petroleum (b. p. 60—80°) gave the epimer as needles (70 mg.), m. p. 154—155° (Found: C, 19·5; H, 1·2; Cl, 69·35%). Evaporation of the filtrate gave a semi-solid (2·42 g.) which, on crystallisation from light petroleum (b. p. 60—80°) (charcoal), gave the pentanol (II) (0·95 g.) as prisms, m. p. 84—85°, undepressed on admixture with authentic material.

1,1,1,5,5,5-*Hexachloro*-3,4-*epoxy*-2-*methylpentan*-2-*ol* (IV).—Methylmagnesium iodide [from magnesium (1·6 g.) in ether (100 ml.)] was treated dropwise at 0° with the ketone (III) (20·68 g.) in ether (100 ml.) over 2 hr., stirred for 2 hr., and kept at room temperature overnight. The mixture was treated at 0° with 2N-sulphuric acid (50 ml.), the ethereal layer separated, and the aqueous phase extracted with ether. The combined ether extracts were washed with sodium thiosulphate, sodium hydrogen carbonate solution, and water, and shaken with charcoal and magnesium sulphate. Removal of the ether left a gum, which, on trituration with light petroleum (b. p. 40—60°), deposited a solid (4·53 g.), m. p. 76—77°, probably a mixture of the ketone and its hydrate. The filtrate from this material yielded a solid which crystallised at −20° in light petroleum (b. p. 60—80°) to give the 2-*methylpentan*-2-*ol* (0·41 g.), m. p. 92—93° (Found: C, 22·2; H, 1·5; Cl, 65·3. $C_6H_6Cl_6O_2$ requires C, 22·3; H, 1·9; Cl, 65·9%), $\nu_{max.}$ (CCl_4) 3600 (OH) and 3033 cm.$^{-1}$ (epoxide CH).

2-*Methylpentane*-2,3-*diol Di*-p-*nitrobenzoate*.—The ketone (III) (9·3 g.) in ethanol (250 ml.) was hydrogenated over pre-reduced palladium oxide (1·4 g.), 10% palladium–charcoal (4·6 g.), and anhydrous potassium carbonate (45 g.). The hydrogen uptake was 90% of theory after 4 hr. Removal of the catalyst and solvent left an oil which was dissolved in ether (100 ml.) and tetrahydrofuran (200 ml.), and added to methylmagnesium iodide [from magnesium (2·2 g.) in ether (100 ml.)]. The mixture refluxed and deposited a white solid. It was stirred and refluxed for 0·5 hr. and stored at room temperature overnight. Processing with ammonium chloride solution (25 g. in 50 ml.) gave a gum (0·5 g.) which, with *p*-nitrobenzoyl chloride (2·5 g.) and pyridine (10 ml.), gave the *di*-p-*nitrobenzoate* (40 mg.), m. p. 152—154° (from ethanol) [Found (on sample dried at 100°/1 mm.): C, 58·45; H, 5·3; N, 6·2. $C_{20}H_{20}N_2O_8$ requires C, 57·7; H, 4·8; N, 6·7%). A sample, m. p. 147—148°, prepared from 2-methylpentane-2,3-diol (by hydroxylation [22] of 2-methylbut-2-ene), did not depress the m. p. of the above specimen and the infrared spectra of the two materials were virtually identical.

Reductive Dehalogenation of the Pentanol (II).—The pentanol (II) (1 g.) was reductively dehalogenated as described above for the ketone. After removal of the catalyst the filtrate was divided into two equal portions. One portion was evaporated under reduced pressure to *ca.* 0·5 ml., and reaction with *p*-nitrobenzoyl chloride as before gave a solid (1·46 g.), m. p. 155—160°, after washing with 2N-hydrochloric acid, water, sodium hydrogen carbonate solution, and water. Two crystallisations from 96% ethanol (charcoal) gave erythro-*pentane*-2,3-*diol di*-p-*nitrobenzoate* as pale yellow plates (0·13 g.), m. p. 163—164·5° (Found: C, 56·8; H, 4·5; N, 6·9; CMe, 5·0, $C_{19}H_{19}N_2O_8$ requires C, 56·7; H, 4·5; N, 7·0; 2CMe, 7·5%). The m. p. was undepressed on admixture with authentic material described below, and the infrared spectra of the two compounds were identical. Prepared in the same way, using 3,5-dinitrobenzoyl chloride, *erythro*-pentane-2,3-diol bis-3,5-dinitrobenzoate had m. p. 199—200° (lit.,[4] 207°) (Found: N, 11·1. Calc. for $C_{19}H_{16}N_4O_{12}$: 11·4%).

The second portion of the filtrate from the hydrogenation above was treated with 2% aqueous methanolic 2,4-dinitrophenylhydrazine sulphate (60 ml.) and gave a solid (0·15 g.), m. p. 134—138°. This was separable by fractional crystallisation from benzene–ethyl acetate

[22] Adkins and Roebuck, *J. Amer. Chem. Soc.*, 1948, **70**, 4044.

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into two solids of m. p. 270° and 142—143°. The latter was the 2,4-dinitrophenylhydrazone of acetaldehyde (Found: C, 43·6; H, 3·85; N, 13·9. Calc. for $C_{15}H_{14}N_4O_{10}$: C, 43·9; H, 3·4; N, 13·6%) and was identical with an authentic sample. When the sequence of reactions was repeated using 4 g. of the pentanol (II), chromatography on alumina gave pentane-2,3-dione bis-2,4-dinitrophenylhydrazone (0·22 g.), needles, m. p. 235—237° (from ethyl acetate) (lit.,[23] values range from 261 to 281°) (Found: C, 44·9; H, 3·1; N, 23·7. Calc. for $C_{17}H_{16}N_8O_8$: C, 44·3; H, 3·5; N, 24·3%), $\nu_{max.}$ ($CHCl_3$), 1612, 1591, 1497, 1337, and 1134 cm.$^{-1}$. An authentic sample, m. p. 271—272° (from chloroform–ethanol) (Found: C, 44·2; H, 3·6; N, 23·75%) had $\nu_{max.}$ ($CHCl_3$), 1608, 1591, 1496, 1337, and 1130 cm.$^{-1}$.

The ethanolic solution from reductive dehalogenation of the pentanol (II) (1 g.) was distilled *in vacuo* into 1% aqueous 2,4-dinitrophenylhydrazine sulphate (200 ml.) to give a yellow solid (0·24 g.) which was shown to be acetaldehyde 2,4-dinitrophenylhydrazone by chromatography on Whatman No. 1 paper [methanol as stationary phase and light petroleum (b. p. 100—120°) as moving phase]. The residue from the distillation of ethanol was treated with water (25 ml.) containing sodium metaperiodate (3 g.) and a few drops of 2N-hydrochloric acid. After 2 days, an aliquot showed an uptake of 0·25 mole of periodate per mole of the pentanol (II). The solution was steam-distilled into 0·5% aqueous 2,4-dinitrophenylhydrazine sulphate (200 ml.) to give a yellow solid (0·95 g.) shown by paper chromatography as before to be a mixture of acetaldehyde and propionaldehyde 2,4-dinitrophenylhydrazones (R_F 0·49 and 0·65, respectively). Acetone 2,4-dinitrophenylhydrazone had R_F 0·61.

*Di-*p*-nitrobenzoates of the Pentane-2,3-diols.*—Hydrogenation of pent-2-yne (22·6 g.) over 5% palladium on barium sulphate (0·2 g.) gave *cis*-pent-2-ene (17·24 g.), b. p. 35—36°, $n_D^{22\cdot5}$ 1·3780, which contained *ca.* 30% of the *trans*-isomer, estimated by examination of its infrared spectrum. Hydroxylation of the alkene (7 g.) by the silver acetate–iodine method[24] gave *erythro*-pentane-2,3-diol (2·13 g.), b. p. 94°/12 mm., n_D^{26} 1·4396 (Found: C, 57·5; H, 11·2. Calc. for $C_5H_{12}O_2$: C, 57·7; H, 11·6%). This gave, by the usual method, the erythro-*di-*p*-nitrobenzoate*, feathery needles, m. p. 164—165°, [from light petroleum (b. p. 100—120°)] (Found: C, 56·6; H, 4·75; N, 6·85%). This compound was obtained in an attempt to prepare the *threo*-isomer by reaction of the hydrogen peroxide–formic acid reagent with the above pent-2-ene. In view of this, and to confirm the structure assigned to the *erythro*-compound, *threo*-pentane-2,3-diol *di-*p*-nitrobenzoate* was prepared as follows. Pent-2-yne (20 g.) was converted, by reduction with sodium in liquid ammonia, into *trans*-pent-2-ene (3·7 g.), n_D^{22} 1·4005 and this was changed into *threo*-pentane-2,3-diol (0·55 g.), b. p. 85°/15 mm., by hydroxylation with t-butyl alcohol, hydrogen peroxide, and osmium tetroxide.[25] The diol gave the threo-*di-*p*-nitrobenzoate* as needles, m. p. 128—130° [from light petroleum (b. p. 100—120°)] (Found: C, 56·5; H, 4·45; N, 7·1%). The infrared spectrum of this compound differed from that of the *erythro*-isomer in some details in the 650—1300 cm.$^{-1}$ region.

*Other Di-*p*-nitrobenzoates.*—The following di-*p*-nitrobenzoates were prepared for comparison with that from the pentanol (II) when other structures were under consideration. They were crystallised from aqueous ethanol.

Racemic *pentane-2,4-diol di-*p*-nitrobenzoate* (from the pentane-2,4-diol obtained by sodium borohydride reduction of pentane-2,4-dione), pale yellow needles, m. p. 128—130° (Found: C, 57·2; H, 4·0%). The orientation follows from its identity with the compound obtained from the bromo-diol (V).

*2-Methylbutane-2,3-diol di-*p*-nitrobenzoate*, pale yellow needles, m. p. 179—181° (Found: C, 57·2; H, 4·75; N, 6·8%).

*2-Methylbutane-1,2-diol di-*p*-nitrobenzoate*, pale yellow needles, m. p. 107—109° (Found: C, 56·8; H, 4·8; N, 6·9%).

3-Bromo-1,1,1,5,5,5-hexachloropentane-2,4-diol (racemic form) (V).—The pentanol (II) (15 g.) was heated under reflux with 60% hydrobromic acid (150 ml.) and glacial acetic acid (150 ml.) for 5 hr. (stored at room temperature overnight after 2·5 hr.). The solvents were removed *in vacuo* to give an oil which was poured into saturated sodium hydrogen carbonate solution and extracted with ether. After washing with water and drying ($MgSO_4$), evaporation of the ether gave an oil which gave two solids m. p. 79—81°, (2·57 g.) (Found: C, 16·25; H,

[23] Heilbron, Jones, Smith, and Weedon, *J.*, 1946, 54; Hickinbottom, Peters, and Wood, *J.*, 1955, 274; Rossi and Schinz, *Helv. Chim. Acta*, 1950, **33**, 725.
[24] Gunstone and Morris, *J.*, 1957, 487.
[25] Milas and Sussman, *J. Amer. Chem. Soc.*, 1936, **58**, 1302.

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1·0%) and m. p. 67—70°, (6·43 g.) (Found: C, 16·15; H, 1·1%). The second material (2·99 g.) was suspended overnight in 0·135M-sodium metaperiodate solution (250 ml.) and titration indicated a consumption of 0·00169 moles of the triol (V) with the production of 0·0016 moles of acid: the good agreement of these values meant the absence of any bromo-α-diol. The residual solid was filtered off and recrystallised from light petroleum (b. p. 60—80°) to give the *bromohexachloropentanediol* (0·98 g.), m. p. 77—79° as clusters of rectangular laths (Found: C, 15·8; H, 1·5; total halogen, 72·5. $C_5H_5BrCl_6O_2$ requires C, 15·4; H, 1·3; total halogen, 75·1%), $\nu_{max.}$ (Nujol) 3400 cm.$^{-1}$ (OH). The *acetate*, cubes, had m. p. 90—93° [from light petroleum (b. p. 60—80°)] (Found: C, 23·3; H, 1·6. $C_9H_9BrCl_6O_4$ requires C, 22·8; H, 1·9%), $\nu_{max.}$ (Nujol) 1765 (CO) and 1208 cm.$^{-1}$ (C–O). Refluxing the bromo-diol (0·4 g.) in acetone (20 ml.) with anhydrous potassium acetate (0·492 g.) for 5 hr. gave the pentanol (II) (0·18 g., 56·8%), m. p. 81—84°, undepressed on admixture with authentic material.

Reduction of the Bromohexachloropentanediol (V).—The diol (5 g.) was reductively dehalogenated over palladium–charcoal and potassium carbonate as described previously. At atmospheric pressure hydrogen uptake was sluggish (6·6 l. after 8 hr.) so the reduction was completed (uptake 7·93 l., calc. 10·45 l.) at 50 psi. The product was distilled, b. p. 96—99°/15 mm., n_D^{26} 1·4408, and the infrared spectrum indicated the presence of carbonyl-containing impurities. It yielded racemic pentane-2,4-diol di-*p*-nitrobenzoate as pale yellow needles, m. p. 125—127° (melt cleared at 130°) (from aqueous ethanol) (Found: C, 57·2; H, 4·3, N, 7·4%). The infrared spectrum (Nujol) was virtually identical with that of the sample prepared above and on admixture of the samples the m. p. was 126—129° (softened at 123°). The acetate had b. p. 99—101°/16 mm., n_D^{21} 1·4163 (Found: C, 57·35; H, 8·4. Calc. for $C_9H_{16}O_4$: C, 57·4; H, 8·6%), $\nu_{max.}$ 1735 (CO) and 1240 cm.$^{-1}$ (C–O).

meso-*Pentane*-2,4-*diol Di*-p-*nitrobenzoate*.—The following includes a simplified version of the Dale [8] process for the preparation of *meso*-pentane-2,4-diol cyclic borate. Pentane-2,4-dione (20 g.) in methanol (100 ml.) was stirred and treated dropwise with potassium borohydride (25 g.) in methanol (500 ml.) and water (200 ml.) over 10 min. The temperature rapidly rose to 60°. After stirring at room temperature overnight the solution was evaporated *in vacuo* until solid appeared. Water (50 ml.) was added and the solution was poured into 2N-hydrochloric acid (2315 ml., 1 equiv.) and continuously extracted with ether (8 hr.). The extract was washed with saturated sodium chloride solution, dried ($MgSO_4$), and evaporated to give an oil which yielded the cyclic borate, stout needles (3·0 g.), m. p. 81—82° [from benzene–light petroleum (b. p. 40—60°) (1 : 4) at 0°] (lit.,[8] 82—83°). This compound was refluxed in methanol (100 ml.) and concentrated sulphuric acid (2 ml.) for 1 hr. The methanol was distilled off until the distillate failed to give a positive flame test for borate. Methanol (100 ml.) was added, the solution was shaken with barium carbonate and filtered, and the filtrate evaporated to yield an oil. The oil, with *p*-nitrobenzoyl chloride and pyridine as before, gave *meso*-pentane-2,4-diol di-*p*-nitrobenzoate as pale yellow flakes, m. p. 155—157° (from aqueous ethanol) (Found: C, 56·9; H, 4·6; N, 6·9%). The infrared spectrum (in $CHCl_3$) differed from that of the racemic isomer in the 900—1000 cm.$^{-1}$ region.

1,1,1,5,5,5-*Hexachloropentane*-2,3,4-*triol* (VIII).—The pentanol (II) (1 g.) (or its acetate) was refluxed for 5·5 hr. with concentrated hydrochloric acid (10 ml.) and glacial acetic acid (10 ml.). The solvent was evaporated under reduced pressure, the residue washed in ether with sodium hydrogen carbonate and water. The ether was evaporated in the presence of benzene to give an oil which yielded the *triol* as colourless microrhombs (90 mg.), m. p. 116—118° [from light petroleum (b. p. 60—80°)] (Found: C, 19·0; H, 1·8; Cl, 64·2; active H, 0·85. $C_5H_6Cl_6O_3$ requires C, 18·3; H, 1·85; Cl, 65·1; active H, 0·9%), $\nu_{max.}$ (Nujol) 3340, 3415, 3312 (OH), 2952, and 2963 cm.$^{-1}$ (CH). In another experiment the pentanol (II) (2 g.) gave the triol (VIII) (0·4 g.), and distillation of the mother-liquor gave an oil (0·52 g.), b. p. 124°/0·9 mm., $n_D^{25\cdot3}$ 1·5311 (Found: C, 19·3; H, 1·6%), which solidified to give the pentanol (II), m. p. 82—84°, undepressed on admixture with authentic material. Catalytic dehalogenation (hydrogen uptake 90·7% of theory) of the triol (VIII) gave an impure sample of pentane-2,3,4-triol (16·5%), b. p. 120°/1·75—2·5 mm. Reaction of this material (0·32 g.) with *p*-nitrobenzoyl chloride gave *pentane*-2,3,4-*triol tri*-p-*nitrobenzoate*, pale yellow needles (0·23 g.), m. p. 167—170° (softening at 162°) (from ethanol) (Found: C, 55·2; H, 3·8, N, 7·9; CMe, 1·7. $C_{26}H_{21}N_3O_{12}$ requires C, 55·0, H, 3·7; N, 7·4; CMe, 5·3%).

Periodate Oxidation.—The triol (VIII) (6 g., 0·01835 mole) was dissolved in 0·1346M-sodium metaperiodate (500 ml.) and kept at room temperature in the dark. Titration of aliquots

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showed the reaction to be virtually complete after 30 min. and, after 4 days, 1·88 moles of periodate per mole of compound had been consumed. Titration of aliquots with 0·1N-sodium hydroxide (Methyl Red indicator) indicated 0·93 moles of acid per mole of triol had been liberated. In a small-scale oxidation some of the water was distilled away from the reactants and a test with chromotropic acid [26] showed the presence of formic acid in the distillate.

The Triol (VIII) *Mono- and Tri-acetates* (with A. C. WHITE).—(*a*) The triol (VIII) (0·61 g.) was kept at 100° for 3 hr. with acetic anhydride (5 ml.). Removal of the reagent under reduced pressure gave an oil which solidified on trituration with light petroleum (b. p. 40—60°) to yield the *monoacetate* (0·14 g.), m. p. 153—160° (Found: C, 23·5; H, 2·5; Cl, 58·0. $C_7H_8Cl_6O_4$ requires C, 22·8; H, 1·9; Cl, 57·7%), $\nu_{max.}$ (Nujol) 3378 (OH) and 1736 cm.$^{-1}$ (acetate CO).

(*b*) The pentanol (II) (4·9 g.) was kept for 7 days at 0° in 50% hydrogen bromide in acetic acid (24 ml.) and then at 100° for 1 hr. The solution was poured into water and extracted with ether which was washed with sodium hydrogen carbonate solution and dried ($MgSO_4$), and the ether evaporated. Crystallisation of the residue from light petroleum (b. p. 60—80°) gave the monoacetate as colourless microrhombs, m. p. 163—165° (softened 155°) (Found: Cl, 57·75%). The infrared spectrum (Nujol) was identical with that of the monoacetate above. Evaporation of the filtrate from the crystallisation gave an oil (3·5 g.), b. p. 135—140°/0·5—0·55 mm. (Found: C, 20·7; H, 1·8; Cl, 61·3%), $\nu_{max.}$ 3435 (OH), 1745s 1615w, and 1210s cm.$^{-1}$.

The triol (VIII) (4·45 g.) in acetic anhydride (25 ml.) and 70% perchloric acid (3 drops) was refluxed for 10 min. and glacial acetic acid (10 ml.) added. After 16 hr. at 20° the solution was poured into ice–water to give a solid (5·92 g.), m. p. 114—116°. Recrystallisation from light petroleum (b. p. 60—80°) gave the *triacetate* as needles, m. p. 118—119° (Found: C, 29·8; H, 2·5; Cl, 47·0; CMe; 9·2. $C_{11}H_{12}Cl_6O_6$ requires C, 29·2; H, 2·7; Cl, 47·0; 3CMe, 10·0%).

The Triol Monobenzoate (IX).—The pentanol (II) benzoate (1·06 g.) was refluxed in concentrated hydrochloric acid (10 ml.) and glacial acetic acid (10 ml.) for 4·75 hr. After 16 hr. at room temperature the solution was evaporated under reduced pressure to leave a solid which was washed in ether with sodium hydrogen carbonate and water, dried ($MgSO_4$), and the ether distilled to give colourless microneedles (0·53 g.). Crystallisation from aqueous ethanol gave the *monobenzoate* (0·1 g.) as white needles, m. p. 159—160° (Found: C, 33·7; H, 2·6; Cl, 48·4; active H, ($LiAlH_4$) 0·7. $C_{12}H_{10}Cl_6O_4$ requires C, 33·4; H, 2·3; Cl, 49·4; active H, 0·4%), $\nu_{max.}$ (Nujol) 3504 (OH), 1715 (CO), and 1270 cm.$^{-1}$ (C–O) [cf. benzoate CO frequency at 1740 cm.$^{-1}$ for the pentanol (II) benzoate].

The Cyclic Sulphate (X).—The finely powdered pentanol (II) (5 g.) was added to concentrated sulphuric acid (20 ml.). After 30 min. at room temperature the clear solution was poured on to crushed ice. The crude product separated as a viscous oil which rapidly crystallised to give the *cyclic sulphate* as colourless prisms (3·5 g.) m. p. 149—150° (from aqueous ethanol), pK_a 4·5 in 50% EtOH (decomposes with N-NaOH), [Found: C, 16·6; H, 1·6; Cl, 57·4; S, 9·0%; *M* (Rast), 389. $C_5H_4Cl_6O_5S$ requires C, 16·3; H, 1·1, Cl, 57·6; S, 8·7%, *M* 368], $\nu_{max.}$ 3625 (OH) and 1220 cm.$^{-1}$ (O·SO_2·O). N.m.r. spectrum: doublet at 6·08 τ (OH), quadruplet (triplet?) at 5·27 τ (H-2), quadruplet at 4·63 τ (H-3), doublet at 4·31 τ (H-4). The low coupling constant ($J_{2,3}$ = 2·5 c./sec.) suggests that the 2- and 3-protons may be *trans*-related. The compound was recovered unchanged after refluxing for 5 hr. in concentrated hydrochloric–acetic acid. The acetate (0·75 g.) [from the alcohol (1 g.) in acetic acid–acetic anhydride (10 ml. of each) with 70% $HClO_4$ (2 drops) for 2 days] formed parallelepipeds, m. p. 112—114° [from light petroleum (b. p. 60—80°)] (Found: C, 19·8; H, 1·6; Cl, 48·6. $C_7H_6Cl_6O_6S$ requires C, 19·5; H, 1·4; Cl, 49·4%), $\nu_{max.}$ (Nujol) 1775 (CO) 1412 (O·SO_2·O), 1222, and 1189 cm.$^{-1}$ (O·SO_2·O and acetate C–O).

1,1,1,5,5,5-*Hexachloro*-3,4-*dihydroxypentan*-2-one (XI).—The ketone(III)–hydrate mixture of m. p. 75—77° (5 g.) was powdered under concentrated sulphuric acid (40 ml.) and kept at room temperature for 11 days with occasional shaking. Almost all the material dissolved. The mixture was filtered and the filtrate poured on to crushed ice to give an oil which was extracted with ether (4 × 50 ml.). The ether was washed with sodium hydrogen carbonate solution and saturated sodium chloride solution, dried (Na_2SO_4), and evaporated. The residue yielded the *hexachlorodihydroxypentanone*, irregular off-white flakes (0·45 g.), m. p. 127—128° [from light petroleum (b. p. 60—80°)] (Found: C, 18·55; H, 1·3; Cl, 64·8. $C_5H_4Cl_6O_3$ requires C, 18·5; H, 1·2; Cl, 65·5%), $\nu_{max.}$ (Nujol) 3400 (OH) and 1740 cm.$^{-1}$ [CCl_3(CO)].

[26] Feigl, " Spot Tests," transl. Oesper, Elsevier, New York, 1947, p. 397.

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Synthesis of 1,1,1,5,5,5-*Hexachloro*-3,4-*epoxypentan*-2-*ol* (VII).—1,1,1,5,5,5-Hexachloro-4-hydroxypentan-2-one [12] (32·77 g.) was stirred and heated at 100° for 5 hr. with bromine (24 g.). Hydrogen bromide was evolved. After standing at room temperature overnight, the bromine-coloured mixture was washed in ether with sodium hydrogen carbonate, sodium pyrosulphite, sodium hydrogen carbonate, and water, and dried ($MgSO_4$). After evaporation of the ether and distillation of the residue, the fraction (13·22 g.) of b. p. 148—154°/3 mm. was again reacted with bromine (4 ml.) for 24 hr., processed as before, and distilled through a 4 cm. Fenske column to give 3-*bromo*-1,1,1,5,5,5-*hexachloro*-4-*hydroxypentan*-2-*one* (XV) (2·1 g.), b. p. 114°/0·25 mm., n_D^{25} 1·5503 (Found: C, 15·5; H, 0·7; total halogen, 73·0. $C_5H_3BrCl_6O_2$ requires C, 15·5; H, 0·8; total halogen, 75·5%), $\nu_{max.}$ 3460s (OH) and 1750s cm.$^{-1}$ (CO).

The above bromo-ketol (3·88 g.) (total halogen, 74·0%) in tetrahydrofuran (10 ml.) was stirred and treated with potassium borohydride (0·31 g.) in water (2 ml.), the temperature being kept below 25°. The mixture formed two layers and was stirred at room temperature for 1 hr. More tetrahydrofuran (10 ml.) was added and stirring continued for 0·5 hr. After dilution with water (100 ml.) and acidification with 2N-sulphuric acid, the mixture was extracted with ether. The extract was washed with sodium hydrogen carbonate and ammonium sulphate, dried ($MgSO_4$), and the ether distilled at atmospheric pressure. The residue gave two fractions, b. p. 120—138°/0·4 mm. (0·92 g.) and 138—142°/0·35 mm. (1·17 g.). These yielded, respectively, on trituration with light petroleum (b. p. 40—60°), solid (A) (0·15 g.), m. p. 115—118° and solid (B) (0·47 g.), m. p. 92—94°. Solid (A) (Found: C, 19·2; H, 1·85%) showed similarities in its infrared spectrum with that of the lower-melting isomer of 1,1,1,5,5,5-hexachloropentane-2,4-diol, and was probably a mixture of the two forms of the latter. Crystallisation of solid (B) (0·2 g.) from light petroleum (b. p. 60—80°) gave 3-*bromo*-1,1,1,5,5,5-*hexachloropentane*-2,4-*diol* (XVI) (0·126 g.) as flat microneedles, m. p. 94—96° (Found: C, 15·6; H, 1·5; total halogen, 75·7. $C_5H_5BrCl_6O_2$ requires C, 15·4; H, 1·3; total halogen, 75·1%), $\nu_{max.}$ (Nujol) 3350 cm.$^{-1}$ (OH).

(*a*) The above bromo-diol (0·2 g.) was refluxed for 2·5 hr. in acetone (10 ml.) with anhydrous potassium acetate (0·246 g.). The mixture was evaporated to 5 ml. and water (5 ml.) added. After distillation of the rest of the acetone and cooling, needles (10 mg.), m. p. 151—154°, appeared. Crystallisation from light petroleum (b. p. 60—80°) gave the epimer (VII) of the pentanol (II) as needles, m. p. 154—155°, identical (mixed m. p. and infrared spectrum) with authentic material. Extraction of the above aqueous filtrate with ether gave a solid which yielded rhombs (50 mg.), m. p. 109—116° [from carbon tetrachloride–light petroleum (b. p. 60—80°)] (Found: C, 20·9; H, 2·0%), $\nu_{max.}$ (Nujol) 3375s (OH) and 1715m cm.$^{-1}$ (CO). This was probably an impure sample of 1,1,1,5,5,5-hexachloro-4-hydroxypentane-3-one.

(*b*) The above bromo-ketol (3·88 g.) in propan-2-ol (40 ml.) with aluminium isopropoxide (9·12 g.) was heated at 110—120° until the slow distillate gave a negative test for acetone (2·3 hr.). The solvent was removed under reduced pressure to leave a gum which was treated with 2N-sulphuric acid (164 ml.) and extracted with ether (5 × 80 ml.). After washing with sodium hydrogen carbonate solution and water, and drying (Na_2SO_4), the ether was evaporated to give an oil which, on trituration with light petroleum (b. p. 40—60°), yielded a solid (0·11 g.), m. p. 147—149°) (softening 143—145°). Crystallisation from light petroleum (b. p. 60—80°) gave the epimer (VII) (0·1 g.), m. p. 152—153°, undepressed with authentic material. The infrared spectra were identical. The filtrate from the solid gave two oils, b. p. 118°/0·9 mm. (0·39 g.) and 142—145°/0·4 mm. (1·74 g.), which were not further investigated.

1,1,1,5,5,5-*Hexachloropent*-3-*en*-2-*ol* (XVII).—1,1,1,5,5,5-Hexachloro-4-hydroxypentan-2-one [12] (3·09 g.) was mixed with toluene-*p*-sulphonic acid (1·6 g.) and distilled at atmospheric pressure and then at 20 mm. The distillate solidified, and crystallisation from light petroleum (b. p. 60—80°) gave the ketol (0·17 g.). Evaporation of the filtrate from the crystallisation gave an oil which, on distillation, yielded 1,1,1,5,5,5-*hexachloropent*-3-*en*-2-*one* (0·76 g.), b. p. 123—125°/17 mm., n_D^{20} 1·5321 (Found: C, 22·1; H, 0·9; Cl, 74·1. $C_5H_2Cl_6O$ requires C, 20·7; H, 0·7; Cl, 73·3%), $\nu_{max.}$ 1730 (CO), 1624 (C=C), and 963 cm.$^{-1}$ (*trans*-C=C), $\lambda_{max.}$ 301 (ε 251) and 206 mμ (ε 7730). The same compound, b. p. 127—132°/13 mm., n_D^{22} 1·5300 was obtained when the crude acetate of the ketol was pyrolysed over glass wool at 300—310° and the product redistilled. The infrared spectra of the two materials were identical.

Lithium aluminium hydride reduction of the above ketone in ether at 5° gave impure 1,1,1,5,5,5-hexachloropent-3-en-2-ol (XVII), b. p. 156°/18 mm., n_D^{24} 1·5366 (Found: C, 21·4; H, 1·4. $C_5H_4Cl_6O$ requires C, 20·5; H, 1·3%), $\nu_{max.}$ 3495 (OH), 1736 (CO), and 1618 cm.$^{-1}$ (C=C).

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5,5,5-*Trichloropent*-3-*en*-2-*ol* (XVIII).—5,5,5-Trichloropent-3-en-2-one [27] (24·98 g.) in tetrahydrofuran (50 ml.) was treated dropwise (10 min.) with stirring with lithium borohydride (0·872 g.) in tetrahydrofuran (58·4 ml.), the temperature being kept below 40° by cooling. After stirring for 5 min. the solution was processed as usual to give the *pentenol* (14·44 g.) as a colourless oil, b. p. 88°/3 mm., n_D^{24} 1·5041 (Found: C, 31·7; H, 3·7; Cl, 56·6. $C_5H_7Cl_3O$ requires C, 31·7; H, 3·7; Cl, 56·1%), $\nu_{max.}$ 3350s (OH) 1618s (C=C), and 945 cm.$^{-1}$ (*trans*-C=C). This compound (30 g.) with acetic acid–acetic anhydride–perchloric acid gave the *acetate* (30·25 g.), b. p. 108—110°/17 mm., n_D^{22} 1·4786 (Found: C, 37·6; H, 3·6. $C_7H_8Cl_3O_2$ requires C, 36·4; H, 3·4%).

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[27] Cf. Salkind in " Beilstein's Handbuch," 1st edn., Springer, Berlin, 1918, Vol. I, p. 732.