58. *The Dichlorobutanediols. Part I. The Addition of Hypochlorous Acid to Some Chlorobutenols.*

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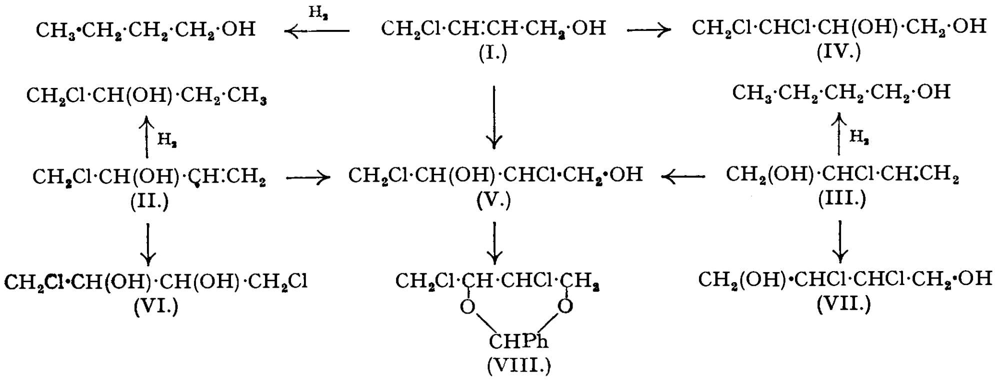
By the action of hypochlorous acid on 2-chlorobut-3-en-1-ol, 2 : 3-*dichlorobutane*-1 : 4-*diol* and 2 : 4-*dichlorobutane*-1 : 3-*diol* have been synthesised, the latter being isolated through its *benzylidene* derivative. Hypochlorous acid reacts with 4-chlorobut-2-en-1-ol and with 1-chlorobut-3-en-2-ol to give 3 : 4-*dichlorobutane*-1 : 2-*diol* and *meso*-1 : 4-dichlorobutane-2 : 3-diol respectively; 2 : 4-dichlorobutane-1 : 3-diol, also, is probably formed in both instances.

1 : 4-Dichlorobutane-2 : 3-diol is known both in the *meso*- and the DL-form. The former, erythritol 1 : 4-dichlorohydrin, was prepared by Henniger (*Ann. Chim. Phys.*, 1886, **7**, 228) by the action of hydrochloric acid on erythritol, whilst the latter, DL-threitol 1 : 4-dichlorohydrin, was obtained by Kilmer, Armstrong, Brown, and du Vigneaud (*J. Biol. Chem.*, 1942, **145**, 495) by oxidation of 1 : 4-dichlorobut-2-ene with potassium permanganate. None of the other three possible structural isomers has been described, and since they were of interest as possible starting materials for the preparation of dihydroxydithiols (Evans, Fraser, and Owen, this vol., p. 248) their synthesis has been studied. The first method of approach involved the investigation of the addition of hypochlorous acid to the three isomeric chlorobutenols (I), (II), and (III), since the four structurally isomeric dichlorobutanediols could theoretically be formed thereby.



4-Chlorobut-2-en-1-ol (I) and 1-chlorobut-3-en-2-ol (II) are both formed by the addition of hypochlorous acid to butadiene, by the use of either calcium hypochlorite at 0° (Kadesch, *J. Amer. Chem. Soc.*, 1946, **68**, 46) or chlorourea at −12° (Petrov, *J. Gen. Chem. Russia*, 1938, **8**, 131). The former method is stated to give a 50% yield of (II) and 19% of (I), and is carried out at rather high dilution, whilst the latter method appears to give only a very small amount of (I). It has been shown by Hanby and Rydon (*J.*, 1946, 114) that *tert.*-butyl hypochlorite can be used in relatively high concentration for the addition of hypochlorous acid to styrene, and by applying this method to butadiene we have obtained an improved yield (24%) of (I), together with 36% of (II). 2-Chlorobut-3-en-1-ol (III) was prepared by reaction of butadiene monoxide with hydrochloric acid (cf. Petrov, *J. Gen. Chem. Russia*, **1941**, **11**, 991; Kadesch, *J. Amer. Chem. Soc.*, 1946, **68**, 41). The structures of these chlorobutenols (characterised as their *α-naphthylurethanes*) were confirmed by hydrogenation over Raney nickel, whereby both (I) and (III) gave *n*-butanol, whilst (II) gave 1-chlorobutan-2-ol, the halogen in which was unexpectedly resistant towards hydrogenolysis.

It is clear from the scheme shown that each of the compounds (I), (II), and (III), by the action of hypochlorous acid, can give two structurally isomeric dichlorobutanediols, in which the chlorine atoms occupy, from (I), positions 3 : 4- and 2 : 4-; from (II), positions 2 : 4- and 1 : 4-; and from (III), positions 2 : 4- and 2 : 3-. Each product, furthermore, can exist in two stereoisomeric forms, so that, in all, four isomers are possible from each reaction; the low yields of crystalline material obtained in some of these reactions can be ascribed to this factor.

From the action of hypochlorous acid, derived from *tert.*-butyl hypochlorite, on (I), a solid of m. p. 69° was obtained, which reacted with one mol. of sodium metaperiodate with liberation of formaldehyde (cf. Jackson and Hudson, *J. Amer. Chem. Soc.*, **1939**, **61**, 1530), indicating the existence of a terminal vicinal pair of hydroxyl groups, and was therefore 3 : 4-*dichlorobutane*-1 : 2-*diol* (IV). The liquid portion of the reaction product consumed only 0·2 mol. of sodium metaperiodate, and probably contained the 2 : 4-dichloro-isomer (V).

1-Chlorobut-3-en-2-ol (II) with hypochlorous acid gave a product from which a small amount of *meso*-1 : 4-dichlorobutane-2 : 3-diol (VI) was isolated, its structure being confirmed by quantitative reaction with sodium metaperiodate. The liquid portion, from its behaviour towards this reagent, again appeared to contain some of the 2 : 4-dichloro-isomer (V).

From the reaction product of 2-chlorobut-3-en-1-ol with hypochlorous acid, 2 : 3-*dichlorobutane*-1 : 4-*diol* (VII) (*diacetate*) was obtained, the structure of which was confirmed by hydrogenolysis to butane-1 : 4-diol. No further solid material could be isolated, and since periodate titration again indicated the presence of the 2 : 4-dichloro-isomer it was decided to attempt the isolation of the latter by reaction with benzaldehyde; it was expected that any remaining 1 : 4-diol would be unaffected, whilst the 2 : 4-dichloro-compound should form a cyclic acetal. This proved to be the case, and by fractional distillation of the condensation product it was possible to isolate the *benzylidene* compound (VIII). This was hydrolysed with aqueous-alcoholic hydrochloric acid to give an oil which partly crystallised and furnished 2 : 4-*dichlorobutane*-1 : 3-*diol* (V), which was stable towards periodate. It is not possible at present to say whether this substance has the *erythro*- or the *threo*-configuration, and the same uncertainty applies also to the isomers (IV) and (VII), although (VII), for reasons discussed in Part II (following paper), is likely to be the *erythro*- (*i.e.*, *meso*-) form.

EXPERIMENTAL.

2-Chlorobut-3-en-1-ol, b. p. 67—69°/29 mm., $n_D^{27°}$ 1·4635, was prepared from butadiene monoxide by the method of Kadesch (*loc. cit.*). The *α-naphthylurethane* crystallised from light petroleum (b. p. 60—80°) in needles, m. p. 81° (Found : C, 65·3; H, 5·1. $C_{15}H_{14}O_2NCl$ requires C, 65·3; H, 5·1%).

Addition of Hypochlorous Acid to Butadiene.—A solution of butadiene (50 g.) in chloroform (100 c.c.) was suspended in a solution of acetic acid (50 c.c.) in water (500 c.c.) contained in a three-necked flask, fitted with tap funnel, mercury-sealed stirrer, and reflux condenser (cooled with alcohol–solid carbon dioxide). The flask was cooled in a freezing mixture, so that the contents were kept at *ca.* 0° while *tert.*-butyl hypochlorite (50 g., crude) was added during 1·5 hours (cf. Hanby and Rydon, *loc. cit.*). After being stirred at 0° for a further hour, the mixture was neutralised with sodium hydrogen carbonate, and the chloroform layer removed. The aqueous portion was extracted again with chloroform, and the combined extracts, after being dried (Na_2SO_4), were evaporated to an oil which on fractional distillation through a 12-inch Fenske column gave 1-chlorobut-3-en-2-ol (18 g.), b. p. 64°/30 mm., $n_D^{16°}$ 1·4652, the *α-naphthylurethane* of which crystallised from light petroleum (b. p. 60—80°) in micro-needles, m. p. 91—92° (Found: C, 65·4; H, 5·2. $C_{15}H_{14}O_2NCl$ requires C, 65·3; H, 5·1%). A higher-boiling fraction (12 g.), b. p. 66—68°/2 mm., $n_D^{18°}$ 1·4832, consisted of 4-chlorobut-2-en-1-ol, giving an α-naphthylurethane, m. p. 94° (Kadesch, *J. Amer. Chem. Soc.*, 1946, **68**, 41, gives m. p. 88—90°).

Hydrogenation of the Chlorobutenols.—(*a*) 2-Chlorobut-3-en-1-ol (2·5 g.) dissolved in methanol (30 c.c.) containing anhydrous potassium acetate (2·0 g.) was hydrogenated over Raney nickel at ordinary temperature and pressure. Absorption of hydrogen (2 mols.) was complete in 3 hours, and after removal of catalyst the methanol was distilled off through a 6-inch Vigreux column. The residue was dissolved in saturated ammonium sulphate solution (50 c.c.) and extracted with ether, the extracts then being dried (Na_2SO_4) and evaporated, to yield *n*-butanol (1·2 g.), b. p. 114—122°, $n_D^{31°}$ 1·3945, characterised as the α-naphthylurethane, m. p. and mixed m. p. 70°.

(*b*) 1-Chlorobut-3-en-2-ol (2·7 g.), under similar conditions took up only 1·1 mols. of hydrogen, and gave 1-chlorobutan-2-ol (1·9 g.), b. p. 140—144°, $n_D^{20°}$ 1·4400. This was identified by oxidation in acetone solution with chromic acid, under the usual conditions, to chloromethyl ethyl ketone (1·6 g.), b. p. 135—138°, $n_D^{15°}$ 1·4342, which gave a semicarbazone, m. p. 123° (lit., 121°), and a phenylhydrazone, m. p. 214° (decomp.) (lit., decomp. 210—215°).

(*c*) 4-Chlorobut-2-en-1-ol (2·2 g.) under similar conditions absorbed 2 mols. of hydrogen, and gave *n*-butanol (1·0 g.), b. p. 110—125°, $n_D^{20^\circ}$ 1·3995, characterised as the α-naphthylurethane, m. p. 69° undepressed on admixture with an authentic sample of m. p. 70°.

Addition of Hypochlorous Acid to 4-*Chlorobut*-2-*en*-1-*ol.*—The olefin (45 g.) was suspended in a mixture of acetic acid (50 c.c.) and water (500 c.c.), and vigorously stirred while *tert.*-butyl hypochlorite (55 g.) was gradually added during one hour, the temperature being kept below 15°. After being stirred for a further 2 hours, the solution was neutralised with sodium hydrogen carbonate, and then saturated with ammonium sulphate and extracted with ether. Removal of ether from the dried (Na_2SO_4) extracts gave a viscous liquid which distilled at 115—130°/6 mm., and partly solidified on standing. The solid (20·6 g.) on recrystallisation from ethyl acetate–light petroleum (b. p. 40—60°) gave colourless plates of 3 : 4-*dichlorobutane*-1 : 2-*diol*, m. p. 69° (Found : Cl, 44·7. $C_4H_8O_2Cl_2$ requires Cl, 44·6%). A portion of this compound, on treatment with aqueous M/16-sodium metaperiodate, took up 0·92 mol. of the reagent (constant value in 40 hours) and gave formaldehyde, identified as the dimedone derivative, m. p. 188°, by aeration of the final solution and passage of the gases through dimedone reagent. The liquid portion (10·5 g.) of the distilled material was found by periodate titration to contain a further 2·5 g. of the vicinal diol, and although its chlorine content (Found : 50·0%) suggested the presence of a little trichlorobutanol (Calc. for $C_4H_7OCl_3$: Cl, 60·0%), the low periodate titre is probably explicable on the basis of the occurrence, in the remaining 8 g., of a considerable proportion of the 2 : 4-dichloro-1 : 3-diol.

Addition of Hypochlorous Acid to 1-*Chlorobut*-3-*en*-2-*ol.*—The olefin (75 g.), acetic acid (100 c.c.), and water (750 c.c.) were treated as above with *tert.*-butyl hypochlorite (90 g.). The product was distilled and collected in six fractions between 100° and 130°/8 mm., $n_D^{15^\circ}$ 1·5012—1·4960, there being no sharp separation. On standing, all the fractions deposited a small quantity of solid. This was collected (5·5 g.) and recrystallised from methanol to give cubes of 1 : 4-dichlorobutane-2 : 3-diol, m. p. 126°, a portion of which reacted with 1·0 mol. of sodium metaperiodate (constant value in 40 hours). The oil (56 g.) remaining after removal of the solid was found by periodate titration to contain only a further 8·4 g. of the vicinal diol (including its stereoisomer, which may also have been present); its chlorine content (Found : 44·3. Calc. for $C_4H_8O_2Cl_2$: Cl, 44·6%) indicated that it probably consisted largely of the 1 : 3-isomer.

Addition of Hypochlorous Acid to 2-*Chlorobut*-3-*en*-1-*ol.*—The olefin (150 g.), suspended in water (1000 c.c.) containing acetic acid (150 c.c.), was treated as above with *tert.*-butyl hypochlorite (170 g.). The product distilled as a colourless oil, b. p. 120—140°/4 mm., which partly solidified on standing. Recrystallisation of the solid from methanol gave needles (27 g.) of 2 : 3-*dichlorobutane*-1 : 4-*diol*, m. p. 119° (Found : C, 30·5; H, 5·2. $C_4H_8O_2Cl_2$ requires C, 30·2; H, 5·1%). The *diacetate*, prepared by heating 12 g. with acetic anhydride (45 c.c.) and concentrated hydrochloric acid (4·5 c.c.) for 2 hours at 95°, and precipitation in water, crystallised from methanol in small prisms (18 g.), m. p. 72° (Found : C, 39·6; H, 5·1. $C_8H_{12}O_4Cl_2$ requires C, 39·5; H, 5·0%). Hydrogenation of the dichloro-diol (2·5 g.) in methanol (20 c.c.) containing potassium acetate (3·5 g.) proceeded slowly in the presence of Raney nickel, 1·8 mols. of hydrogen being absorbed in 2 days. The product, on distillation, furnished butane-1 : 4-diol (0·6 g.), characterised as the bisphenylurethane, m. p. 183° (lit., 183°).

The syrup (85 g.), remaining after collection of the solid dichloro-diol, was heated with benzaldehyde (100 g.) for 2 hours at 90°/80 mm., a slow stream of dry hydrogen chloride being passed in through a capillary inlet, whilst water was allowed to distil. After cooling, the mixture was diluted with ether (400 c.c.), washed with aqueous sodium carbonate, dried (K_2CO_3), and evaporated to an oil, which on distillation gave two main fractions : (i) 28·0 g., b. p. 117—130°/1 mm., $n_D^{15^\circ}$ 1·5180; and (ii) 44·0 g., b. p. 135—137°/0·5 mm., $n_D^{15^\circ}$ 1·5470. (i) was mainly unreacted dichloro-diol (Found : Cl, 40·2. Calc. for $C_4H_8O_2Cl_2$: Cl, 44·6%), whilst (ii) was the *benzylidene* compound of 2 : 4-dichlorobutane-1 : 3-diol (Found : Cl, 29·2. $C_{11}H_{12}O_2Cl_2$ requires Cl, 28·7%).

The benzylidene compound (35 g.) in 50% aqueous alcohol (500 c.c.) and concentrated hydrochloric acid (2 c.c.) was heated at 80° for an hour, and then neutralised with potassium carbonate and evaporated to dryness. The residue was extracted with ether to give an oil (8·6 g.), b. p. 98°/0·1 mm., $n_D^{20^\circ}$ 1·5065, which solidified, and on crystallisation from ethyl acetate–light petroleum (b. p. 40—60°) gave colourless plates of 2 : 4-*dichlorobutane*-1 : 3-*diol*, m. p. 62° (Found : C, 30·5; H, 5·1. $C_4H_8O_2Cl_2$ requires C, 30·2; H, 5·1%), which was stable towards sodium metaperiodate under the usual conditions. It formed a liquid *diacetate*, b. p. 153°/18 mm., $n_D^{23^\circ}$ 1·4605 (Found : C, 40·0; H, 5·0. $C_8H_{12}O_4Cl_2$ requires C, 39·5; H, 5·0%).

Thanks are due to the Medical Research Council for a grant.

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[*Received, April 29th,* 1948.]