59. *The Dichlorobutanediols. Part II.*

By L. N. Owen.

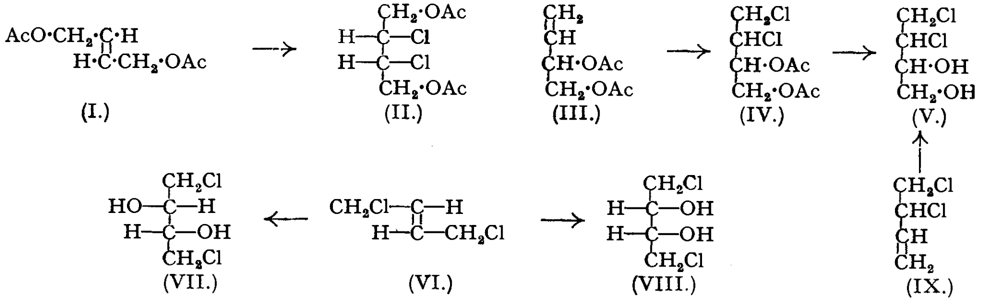
Addition of chlorine to *trans*-1 : 4-diacetoxybut-2-ene and to 1 : 2-diacetoxybut-3-ene gives *meso*-2 : 3-dichloro-1 : 4-diacetoxybutane and 3 : 4-*dichloro*-1 : 2-*diacetoxybutane* respectively, the latter being a mixture of stereoisomers. Hydroxylation of *trans*-1 : 4-dichlorobut-2-ene with potassium permanganate gives DL-1 : 4-dichlorobutane-2 : 3-diol, whilst with performic acid the *meso*-isomer is obtained. Hydroxylation of 1 : 2-dichlorobut-3-ene with either reagent gives a mixture of stereoisomeric 3 : 4-dichlorobutane-1 : 2-diols, one of which is isolated as a solid. *meso*-1 : 4-Dibromobutane-2 : 3-diol is conveniently obtained by hydroxylation of *trans*-1 : 4-dibromobut-2-ene with performic acid.

In Part I (previous paper) it was shown that each of the four structurally isomeric dichlorobutanediols could be obtained by the reaction of hypochlorous acid with an appropriate chlorobutenol. Alternative methods of approach to three of these compounds have now been investigated; they involve addition of chlorine to a diacetoxybutene, and hydroxylation of a dichlorobutene.

1 : 4-Diacetoxybut-2-ene, which, as usually prepared from 1 : 4-dibromobut-2-ene, is the *trans*-compound (I), is known to give on treatment with bromine a 2 : 3-dibromo-1 : 4-diacetoxybutane to which the *meso*-configuration has been assigned, since on reaction with silver acetate it gives erythrityl tetra-acetate (Griner, *Bull. Soc. chim.*, 1893, **9**, 219). By a similar reaction with chlorine, a crystalline 2 : 3-dichloro-1 : 4-diacetoxybutane has now been obtained, identical with that described in Part I; from analogy with the dibromo-compound it presumably has the erythritol configuration (II), which would also be expected on the basis of a *trans*-addition of halogen to the *trans*-olefin.

In the addition of chlorine to 1 : 2-diacetoxybut-3-ene (III) two stereoisomeric products are possible, since the question of *cis*- or *trans*-addition of halogen does not arise. A liquid 3 : *4-dichloro-*1 : *2-diacetoxybutane* (IV) was obtained, which on deacetylation yielded the same 3 : 4-dichlorobutane-1 : 2-diol (V) as that described in Part I, together with a liquid portion which presumably contained the stereoisomer.

The oxidation of *trans*-1 : 4-dichlorobut-2-ene (VI) with potassium permanganate has been reported by Kilmer, Armstrong, Brown, and du Vigneaud (*J. Biol. Chem.*, 1942, **145**, 495) to give a 35% yield of DL-1 : 4-dichlorobutane-2 : 3-diol (VII). By carrying out this *cis*-hydroxylation under rather milder conditions, it has now been possible to raise this yield to 59% (*diacetate*). Furthermore, when the hydroxylation was carried out by the performic acid method (cf. Swern, Billen, and Scanlan, *J. Amer. Chem. Soc.*, 1946, **68**, 1505), which results in *trans*-addition, *meso*-1 : 4-dichlorobutane-2 : 3-diol (VIII) was obtained (*diacetate*).


(I.) (II.) (III.) (IV.) (V.)

(VII.) (VI.) (VIII.) (IX.)

In the hydroxylation of 1 : 2-dichlorobut-3-ene (IX), the possibility of *cis*- or *trans*-addition to the olefinic linkage is ruled out, and two stereoisomeric products are thus possible from the use of either reagent. This has proved to be the case, since with either potassium permanganate or performic acid a semi-solid product was obtained, the solid portion of which proved in both instances to be the same 3 : 4-dichlorobutane-1 : 2-diol (V) as that already prepared by the other route. The liquid portion was shown by reaction with sodium metaperiodate to consist essentially of a vicinal diol, and therefore must have contained the stereoisomer, but no crystalline derivatives could be obtained.

In view of the successful oxidation of *trans*-1 : 4-dichlorobut-2-ene with performic acid, the oxidation of *trans*-1 : 4-dibromobut-2-ene with this reagent was investigated. It was found to take place less smoothly than with the dichloro-compound, to give *meso*-1 : 4-dibromobutane-2 : 3-diol, in rather poor yield. This method is nevertheless more convenient than that described in the literature, which involves the treatment of erythritol with hydrogen bromide (Champion, *Z. Chem.*, 1871, 348).

EXPERIMENTAL.

1 : 4-Diacetoxybut-2-ene was prepared from butadiene, *via* the mixed dibromides, as described by Prévost (*Ann. Chim.*, 1928, **10**, 407). 1 : 2-Diacetoxybut-3-ene was prepared from butadiene monoxide (Evans, Fraser, and Owen, this vol., p. 248).

Details of the preparation of 1 : 2-dichlorobut-3-ene and 1 : 4-dichlorobut-2-ene as given in the literature are somewhat incomplete (cf. Muskat and Northrup, *J. Amer. Chem. Soc.*, 1930, **52**, 4043; Petrov and Sopov, *J. Gen. Chem. Russia*, 1945, **15**, 981). The following procedure has been found satisfactory. To a cooled, stirred solution of butadiene (180 g.) in dry carbon tetrachloride (350 c.c.), a deficiency of chlorine (150 g.) dissolved in the same solvent (750 c.c.) was gradually added during 45 minutes, the temperature being kept below −5° by external cooling (solid carbon dioxide in alcohol).

After removal of most of the solvent, the residue was fractionally distilled at ordinary pressure through an 18-inch Fenske column. 1 : 2-Dichlorobut-3-ene (35 g.) was collected at 123°/766 mm.; it had $n_{D}^{20^\circ}$ 1·4630 (Muskat and Northrup, *loc. cit.*, give b. p. 115°/760 mm., $n_{D}^{30^\circ}$ 1·4550). 1 : 4-Dichlorobut-2-ene (70 g.) had b. p. 159°/766 mm., $n_{D}^{20^\circ}$ 1·4887, and solidified on cooling in ice; it had m. p. 3° (Muskat and Northrup, *loc. cit.*, give b. p. *ca.* 145°/760 mm., $n_{D}^{30^\circ}$ 1·4745; Petrov and Sopov, *loc. cit.*, give $n_{D}^{20^\circ}$ 1·4890).

Addition of Chlorine to 1 : 4-*Diacetoxybut*-2-*ene*.—The diacetate (17·5 g.) was dissolved in carbon tetrachloride (30 c.c.) and cooled to −20°. A solution of chlorine (7·5 g.) in carbon tetrachloride (55 c.c.) was added during 10 minutes, with stirring, the temperature being kept below −10°. After a further 5 minutes, the slight excess of chlorine was destroyed by shaking with aqueous sodium hydrogen sulphite; the carbon tetrachloride layer was then washed with water, dried ($CaCl_2$), and evaporated to an oil which on distillation furnished a main fraction (9 g.), b. p. 85—90°/0·001 mm., which partly solidified. The solid (4 g.) was freed from oil on porous tile, and then recrystallised from methanol to give large prisms of 2 : 3-dichloro-1 : 4-diacetoxybutane, m. p. and mixed m. p. 72° (cf. Part I).

Addition of Chlorine to 1 : 2-*Diacetoxybut*-3-*ene*.—The diacetate (17·2 g.) was treated with chlorine (7·5 g.) under the same conditions as those described above. On distillation, a main fraction (6·3 g.), b. p. 82—92°/0·001 mm., $n_{D}^{15^\circ}$ 1·4640, of 3 : 4-*dichloro*-1 : 2-*diacetoxybutane* was obtained (Found : Cl, 28·7. $C_8H_{12}O_4Cl_2$ requires Cl, 29·2%). A portion of this (3·7 g.) was refluxed in N-methanolic hydrogen chloride (20 c.c.) for 2 hours; after neutralisation with silver carbonate, the filtered solution was evaporated to an oil, which distilled at 90—105°/0·01 mm. (yield, 1·6 g.), and partly crystallised. The solid 3 : 4-dichlorobutane-1 : 2-diol, freed from oil on porous tile, crystallised from chloroform–carbon tetrachloride in leaflets (0·4 g.), m. p. and mixed m. p. 69°.

Oxidation of 1 : 4-*Dichlorobut*-2-*ene*.—(*a*) *With potassium permanganate.* The dichloro-compound (20 g.) was dissolved in ethanol (300 c.c.) and kept at −15° during the gradual addition of a solution of potassium permanganate (20 g.) and magnesium sulphate (15 g., anhydrous) in water (400 c.c.). Sodium hydrogen sulphite (30 g.) dissolved in water was then added, followed by sufficient 4N-sulphuric acid to make the clear solution acid to Congo-red. The solution was then concentrated under reduced pressure to *ca.* 150 c.c. and extracted thrice with ether. Evaporation of the dried (Na_2SO_4) extracts gave a solid residue (15 g.) of DL-1 : 4-dichlorobutane-2 : 3-diol, which crystallised from benzene–light petroleum (b. p. 40—60°) in tufts of needles (12·5 g.), m. p. 62°. A portion of this (5 g.) was heated on the steam-bath for 3 hours with acetic anhydride (25 c.c.) and concentrated hydrochloric acid (1 c.c.); after removal of solvent under reduced pressure the residue was stirred with water (50 c.c.), and yielded a white solid (7·4 g.) which on recrystallisation from methanol gave large prisms of DL-1 : 4-*dichloro*-2 : 3-*diacetoxybutane* (6·5 g.), m. p. 76° (Found : C, 40·0; H, 5·4. $C_8H_{12}O_4Cl_2$ requires C, 39·5; H, 5·0%).

(*b*) *With performic acid.* The dichloro-compound (12 g.) was suspended in pure formic acid (50 c.c.) containing 25% aqueous hydrogen peroxide (15 c.c.) and kept at 45° with frequent agitation. The mixture became homogeneous after 1 hour, and after being kept at 45° overnight gave no reaction with starch–iodide paper. The solution was then diluted with water (50 c.c.), heated on the steam-bath for 10 minutes, and evaporated to dryness under reduced pressure. The solid residue (7·5 g.) was recrystallised from a small amount of hot water to give cubes of *meso*-1 : 4-dichlorobutane-2 : 3-diol (5·5 g.), m. p. 127°. A portion (5 g.) of this was acetylated under the conditions described above for the stereoisomer, and gave meso-1 : 4-*dichloro*-2 : 3-*diacetoxybutane* (7·5 g.), which crystallised from methanol in prismatic clusters, m. p. 117° (Found : C, 39·8; H, 5·2. $C_8H_{12}O_4Cl_2$ requires C, 39·5; H, 5·0%).

Oxidation of 1 : 2-*Dichlorobut*-3-*ene*.—(*a*) *With potassium permanganate.* The dichloro-compound (12 g.) was dissolved in ethanol (180 c.c.) and treated at −15° with a solution of potassium permanganate (12 g.) and magnesium sulphate (10 g.) in water (250 c.c.), by the method already described. After working up in the same way, evaporation of the ethereal extracts gave a semi-solid product (8·5 g.) from which the solid material (4·1 g.) was separated on porous tile. Recrystallisation from chloroform–carbon tetrachloride gave plates of 3 : 4-dichlorobutane-1 : 2-diol, m. p. and mixed m. p. 69°. A portion of the liquid material, on quantitative oxidation with aqueous sodium metaperiodate, consumed 0·96 mol. of the reagent (constant value after 24 hours).

(*b*) *With performic acid.* The dichloro-compound (12 g.) was treated under conditions identical with those described above for the 1 : 4-dichlorobut-2-ene. The solution became homogeneous after 2 hours, and after being kept overnight at 45° it was worked up in the same way to yield an oil, which distilled at 112°/0·5 mm. The distillate (8·1 g.) deposited 2·0 g. of crystals, which on recrystallisation from chloroform–carbon tetrachloride gave 3 : 4-dichlorobutane-1 : 2-diol (1·6 g.), m. p. and mixed m. p. 69°. The liquid portion consumed 0·97 mol. of sodium metaperiodate (constant value after 24 hours).

1 : 4-*Dibromobut*-2-*ene*.—To a stirred solution of butadiene (45 g.) in carbon tetrachloride (500 c.c.), kept at −20°, a solution of bromine (26 c.c.) in carbon tetrachloride (200 c.c.) was added during 45 minutes. Removal of solvent and crystallisation of the residue from light petroleum (b. p. 40—60°) gave 1 : 4-dibromobut-2-ene (72 g.), m. p. 54°.

Oxidation of 1 : 4-*Dibromobut*-2-*ene with Performic Acid*.—The dibromide (30 g.) was suspended in pure formic acid (120 c.c.) containing 25% aqueous hydrogen peroxide (25 c.c.) and kept at 45° with frequent shaking. After 6 hours a homogeneous solution was obtained, which was kept at 45° overnight. The peroxide-free solution was diluted with an equal volume of water, heated on the steam-bath for 30 minutes, and then evaporated under reduced pressure to an oil which partly crystallised. The solid *meso*-1 : 4-dibromobutane-2 : 3-diol (4·1 g.), after being washed with benzene, had m. p. 134°; on acetylation it gave the diacetate, which crystallised from methanol in large prisms, m. p. 137°. The oily portion of the product on distillation furnished two main fractions, (i) 2·8 g., b. p. 80—85°/0·003 mm., and (ii) 2·4 g., b. p. 90—95°/0·003 mm., which were not further investigated.

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