XXIV.—*Properties of Conjugated Compounds. Part VI. The Dibromination Products of Cyclic Butadienes.*

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IN foregoing papers of this series it has been pointed out that the migratory changes displayed by the dibromides of butadienoid hydrocarbons are fundamentally based on the propenoid change $C\!:\!C\cdot C \longrightarrow C\cdot C\!:\!C$. The facile production of 1 : 4-, 1 : 6-, etc., compounds by isomerisation of the corresponding 1 : 2-forms suggests the possibility that all such derivatives of simple conjugated compounds may originate in addition at a single ethylenic linkage and not, wholly or partly, as the result of differential tendencies inherent in the butadienoid structure. It is sought, in continuing the examination of hydrocarbon addition products, to accumulate evidence entirely consistent with additive attack at a single ethylenic centre (whether the mechanism of differential orientation prove finally to be ionic in character or otherwise), and it is shown in this paper that in one instance investigated, namely, that of $\Delta^{1:3}$-*cyclo*hexadiene, this is actually the case. It is reasonable to assume that, in other cases where the issue is not so clear, the lack of definite evidence is due to failure to discover the correct experimental conditions which will enable the 1 : 2-products to be isolated.

Bromination of $\Delta^{1:3}$-cycloHexadiene.—When $\Delta^{1:3}$-*cyclo*hexadiene is dibrominated in hexane or chloroform below $-15°$ and the solvent is removed immediately, without application of heat, a mixture of two isomeric dibromides—a liquid and a solid—is obtained. Each of

these substances passes readily into a third solid isomeride at room temperature or, more rapidly, on heating.   The isomerisation of the original solid form is slow in the dry state (requiring several weeks), that of the liquid more rapid (8% at 15° in 25 hours, 40% at 100° in 15 minutes); both forms change readily when dissolved in a solvent.   If there is delay in working up the bromination product, or if the temperature of the mixture is raised, as, for instance, by distilling off the solvent, partial disappearance of the original forms may occur : indeed the solid form at least may disappear so completely as to become undetectable.   The proportion in which the original bromides appear varies little with the nature of the solvent or with the degree of dilution.

The third isomeride (identical with the *cyclo*hexadiene dibromide obtained by Crossley and Haas, J., 1903, **83**, 498; 1904, **85**, 1403, and by Zelinsky and Gorsky, *Ber.*, 1908, **41**, 2428) is purely a derived form and doubtless represents one of the stereoisomeric forms (I and II).   1 : 4-Dibromides always display a much greater
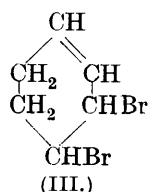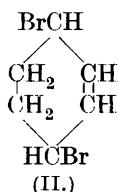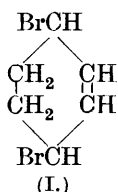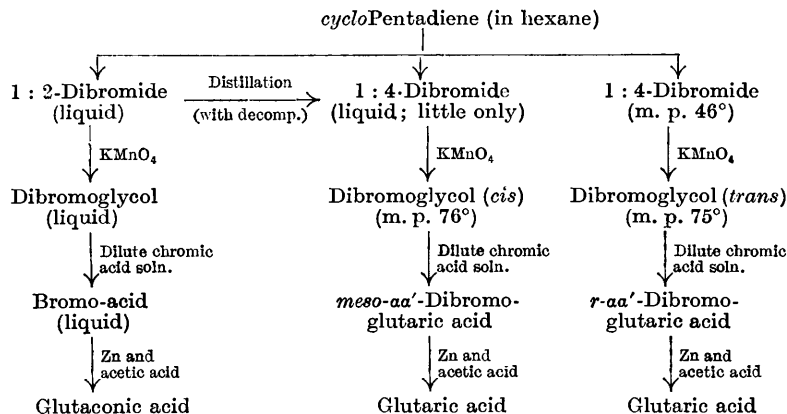

resistance to oxidative degradation than the corresponding 1 : 2-forms :   usually, therefore, the degradation of the latter is too severe to be of value in diagnosing orientation, and that of the 1 : 4-forms follows a normal course.   Here, however, the stability is such that the attack of ozone and of mild oxidising agents is withstood and the molecule breaks down only on drastic treatment which causes complete elimination of halogen.   As might have been anticipated, attempts to convert this dibromide into its diethoxy-derivative with sodium ethoxide resulted only in the production of benzene.   The two original bromides are attacked by ozone and by permanganate so readily that control of degradation is difficult. With the latter reagent the corresponding dibromoglycols are produced in small yield, but the further oxidation cannot be arrested before bromine is eliminated from the molecule.   There can be little doubt, however, that the bromides represent stereoisomeric 1 : 2-forms (III).

Bromination of cyclo*Pentadiene.*—Thiele's investigation of the dibromination of *cyclo*pentadiene (*Annalen*, 1900, **314**, 296) indicates that only 1 : 4-forms are produced :   by bromination in chloroform solution, distillation of the solvent, and fractionation of the bromide

mixture under reduced pressure, he obtained a liquid and a solid *cyclo*pentadiene dibromide; since these were oxidised *via* their respective dibromoglycols to *meso* and *racemic* forms of αα'-dibromoglutaric acid, their 1 : 4-orientation was definitely demonstrated. With the greater part of Thiele's statement we are in complete agreement; if, however, isomerisation during the isolation of dibromides is guarded against, not only is 1 : 4-bromination found to be partial, but interesting dilution and solvent effects on the quantitative relation between the 1 : 2-form and its 1 : 4-isomerides become apparent.

The incidence of the bromination products obtained in *n*-hexane below −15° is shown in the following scheme. The details concerning the degradation products of the two 1 : 4-isomerides are identical with those already given by Thiele. It is also fairly certain that on distillation the liquid 1 : 2-dibromide is converted (with degradation) to a small extent into the solid 1 : 4-form :

*cyclo*Pentadiene (in hexane)

1 : 2-Dibromide (liquid)	Distillation (with decomp.) →	1 : 4-Dibromide (liquid; little only)	1 : 4-Dibromide (m. p. 46°)
KMnO₄		KMnO₄	KMnO₄
Dibromoglycol (liquid)		Dibromoglycol (*cis*) (m. p. 76°)	Dibromoglycol (*trans*) (m. p. 75°)
Dilute chromic acid soln.		Dilute chromic acid soln.	Dilute chromic acid soln.
Bromo-acid (liquid)		*meso-aa'*-Dibromoglutaric acid	*r-aa'*-Dibromoglutaric acid
Zn and acetic acid		Zn and acetic acid	Zn and acetic acid
Glutaconic acid		Glutaric acid	Glutaric acid

preferentially, however, it yields the liquid isomeride. In hexane solution, with increasing dilution the proportion of solid 1 : 4-dibromide isolated from the bromination mixture steadily diminishes, falling, *e.g.*, from 40% to 12% as the final total bromide content increases from 0·28 g. to 2 g. per c.c. of solvent. The effect of substituting chloroform for hexane is drastically to reduce the proportion of solid 1 : 4-form and to increase the total proportion of 1 : 4-dibromide in the bromination product.

EXPERIMENTAL.

Bromination of Δ¹:³-cyclo*Hexadiene.*—The *cyclo*hexadiene was prepared by Hofmann and Damm's method (*Schleischen Kohlenforsch. Kaiser Wilhelm Ges.*, 1925, **2**, 97) from pure *cyclo*hexene and

fractionated over sodium in a stream of carbon dioxide; it had b. p. 80°, $n_D^{16\cdot0°}$ 1·4760, $d_4^{16\cdot0°}$ 0·8421; whence $[R_L]_D = 26\cdot806$.

The bromination was carried out in a flask fitted with a dropping-funnel, a calcium chloride tube, and a stirrer and immersed in a freezing mixture. Usually 8 g. of the hydrocarbon, dissolved in chloroform or, preferably, n-hexane, were brominated at one time. When the theoretical quantity of bromine (diluted) had been added with constant stirring, the solvent was removed as quickly as possible by means of a good vacuum pump, a little light petroleum added to the residue, and the solid bromination product *immediately* separated by strong cooling and filtration. Careful repetitions of the "freezing-out" process and final removal of the solvent (under reduced pressure) from the residual liquor yielded a colourless liquid dibromide.

1 : 2-*Dibromo-*Δ^3-*cyclo*hexene (III). The solid dibromide, after being washed with light petroleum, was usually pure and formed colourless prisms, m. p. 68° (Found : Br, 66·6. $C_6H_8Br_2$ requires Br, 66·6%). Whenever there was delay (for instance, postponement over-night) in isolating the bromination products, in separating the solid dibromide from its liquid isomeride, or in removing crystals of dibromide from a crystallising medium, the m. p. of the crystals obtained was usually about 54° : from such crystals, by rapid fractional crystallisation from light petroleum, small quantities of an isomeric 1 : 4-dibromide, m. p. 108° (see below), could be separated. If the delay in isolating the bromination products was prolonged, there was partial or complete replacement of the solid 1 : 2-dibromide by its isomeride, m. p. 108°.

The liquid dibromide, immediately after isolation, appeared to be free from impurity other than residual traces of its solid stereo-isomeride (Found : Br, 66·4%).

1 : 4-Dibromo-Δ^2-*cyclo*hexene was the sole solid product isolated when there was a delay of 3 days in working up the dibromination mixture, or when heat was applied in the removal of the bromination diluent. It was also directly obtained from the two pure 1 : 2-di-bromo*cyclo*hexenes (see below). It crystallised from light petroleum in colourless prisms, m. p. 108° (Crossley and Haas, *loc. cit.*, give m. p. 108—109°) (Found : Br, 66·7%).

Isomerisation of 1 : 2-*Dibromo*cyclohexene.—The pure *solid* di-bromide suffered gradual isomerisation on standing : after several weeks, complete conversion into 1 : 4-dibromo*cyclo*hexene had occurred. Isomerisation appeared to be accelerated when the dibromide was dissolved in hexane or chloroform and became rapid when the pure dibromide or its solutions were heated.

The *liquid* dibromide isomerised gradually at room temperature and more rapidly on heating ; at 0°, change became perceptible after

2—3 days. The possibility of reversing the 1 :2- $\longrightarrow$ 1 : 4-change at 100° could not be gauged owing to the degradation of the 1 : 4-dibromide when heated for a prolonged period : if the reverse change occurs, it is very slow. On distillation, isomerisation was rapid, the boiling point steadily rising from about 75° to 120°/2 mm.; the fraction of b. p. 110—120°/2 mm., which solidified on cooling, was almost pure 1 : 4-dibromo*cyclo*hexene.

*Oxidation of the Isomeric Dibromo*cyclohexenes.—The stability of the 1 : 4-dibromide, m. p. 108°, frustrated all attempts to oxidise it with permanganate at 0° or at room temperature. The finely powdered bromide was unattacked by cold aqueous chromic acid, but was converted by the hot reagent into succinic acid. The action of ozone was very slow : the bromide suffered change after prolonged ozonisation, but no satisfactory decomposition of the product could be achieved. Nitric acid was equally unsatisfactory as an oxidising agent.

The 1 : 2-dibromide, m. p. 68°, was fairly readily oxidised by permanganate at 0° to the corresponding dibromoglycol, but much of the latter compound suffered further oxidation before the first stage of oxidation was complete. To an acetone solution of 6 g. of the bromide, 60 c.c. of an aqueous solution of permanganate and magnesium sulphate (5% of each) were very slowly added. The manganese mud was filtered off and all acetone removed from both mud and filtrate in a rapid current of air. The mud, suspended in a little water, was just brought into solution by addition of sulphuric acid and sodium bisulphite. The solution, after filtration of a large quantity of unchanged dibromide, was combined with the acetone-free filtrate and extracted ten times with alcohol-free ether. The extract, freed from acid matter by cautious agitation with a few c.c. of saturated bicarbonate solution, was thoroughly dried with sodium sulphate. After evaporation of the ether the residue, 1 : 2-*dibromo*-3 : 4-*dihydroxy*cyclohexane, solidified completely. It separated from petroleum (b. p. 60—80°) in colourless prisms, m. p. 96—98° (Found : Br, 58·1. $C_6H_{10}O_2Br_2$ requires Br, 58·3%). The yield was about 25%, calculated on the bromide taken.

The liquid 1 : 2-dibromide, on oxidation in a similar manner, gave a syrupy glycol containing traces of the above-described dibromoglycol. The latter was extracted with petroleum, but since the liquid glycol decomposed on distillation complete purification could not be effected. The complementary acidic portion of the oxidation product consisted largely of succinic acid.

*Oxidation of the Isomeric Dibromodihydroxy*cyclohexanes.—The most careful treatment with cold aqueous chromic acid or with neutral permanganate failed to prevent loss of bromine, and the

product was invariably succinic acid; no $\alpha\alpha'$-dibromoadipic acid could be obtained.

Bromination of cyclo*Pentadiene.*—The dimeride required for the generation of the hydrocarbon was worked up from " aged " benzene forerunnings as described by Perkins and Cruz (*J. Amer. Chem. Soc.*, 1927, **49**, 517). The carefully fractionated dimeride from certain batches of forerunnings solidified with difficulty on cooling and the crystals, after recrystallisation from alcohol (an operation accomplished with difficulty owing to great solubility), always melted at 19°. The dimeride from other batches was almost completely solid at room temperature and the crystals, which separated easily from strongly cooled alcoholic solution, melted at 32°. The former of these compounds possibly represents a homogeneous modification corresponding to that isolated by Staudinger and Rheiner (*Helv. Chim. Acta*, 1924, **7**, 23) from the intensely cooled liquid portion of commercial di*cyclo*pentadiene. The boiling points of both the lower- and the higher-melting portion were identical (56°/13 mm.); there was no portion boiling above this temperature as recorded by Staudinger and Rheiner. Wieland and Bergel (*Annalen*, 1925, **446**, 19), who separated a liquid dimeride fraction from the di*cyclo*-pentadiene, m. p. 32·5°, also give the b. p. 56°/13 mm. for both portions and state that they could find no trace of Staudinger and Rheiner's " isomeric di*cyclo*pentadiene, b. p. 68—70°/12 mm."

Both the lower- and the higher-melting portion of the dimeride yielded *cyclo*pentadiene when heated with iron filings at 185—190° in the usual way. For the bromination experiments the hydrocarbon was redistilled once (b. p. 42°), precautions being taken to prevent access of moisture.

Bromination in n-*hexane.* Bromination was effected at the temperature of an ice–salt bath, as described above. A deficiency of bromine was always employed in additions to *cyclo*pentadiene and the yields were calculated on the amount of bromine taken. When addition was complete, a solid bromination product was directly frozen out in the usual way. This corresponded to Thiele's *trans*-1 : 4-dibromo-Δ^2-*cyclo*pentene, m. p. 45—46° (Found : Br, 70·9. Calc. : Br, 70·8%). Yield, 40%. Removal of the solvent left an almost colourless liquid consisting mainly of 1 : 2-*dibromo*-Δ^3-cyclo-*pentene*, $d^{20°}$ 1·8867 (Found : Br, 70·6. $C_5H_6Br_2$ requires Br, 70·7%), but containing, as shown by oxidation experiments, a small proportion of *cis*-1 : 4-dibromo-Δ^2-*cyclo*pentene.

Variation of the proportion of diluent employed during bromination affected considerably the amount of the solid dibromide that could be frozen out. The following approximate figures show the relation between the amount of solid isolated and the concentration

of total dibromide (g. per c.c. of solvent employed) in the bromination mixture.

Concentration .... 0·27   0·47   0·67   1·25   2·00
Solid dibromide, % .... 40·0   27·8   27·1   24·0   11·6

Bromination in chloroform. This was effected at the temperature of an ice–salt bath and all precautions against rise in temperature, etc., were taken. The faintly yellow product darkened rapidly as the solvent was removed. On dilution of the chloroform-free product with light petroleum, and strong cooling, less than 2% of solid dibromide could by any means be induced to separate. The dark-coloured liquid dibromide which remained when the solvent was removed was a mixture of 1 : 2-dibromo-Δ³-*cyclo*pentene and *cis*-1 : 4-dibromo-Δ²-*cyclo*pentene.

Isomerisation of cyclo*Pentadiene Dibromides.*—The liquid dibromide ($d^{20°}$ 1·8977) obtained from chloroform solutions of the hydrocarbon distilled with considerable decomposition. The product was a pale yellow liquid (b. p. 68—80°/5 mm.; yield, 82%) which could be redistilled with only slight decomposition. When, in the first distillation, the highest-boiling fraction was retained in the distilling flask and extracted with petroleum, crystals of the solid dibromide, m. p. 45°, were obtained (yield, less than 10%). It is not certain to what extent this was formed during distillation : the solid dibromide is apparently much more soluble in the corresponding liquid 1 : 4-dibromide than in its liquid 1 : 2-isomeride and some proportion of this yield is possibly attributable to incomplete separation at the outset. After several distillations a stable, constant-boiling fraction, b. p. 72°/5 mm., 82°/15 mm., $d^{20°}$ 1·9198 (Found : C, 26·6 ; H, 2·7 ; Br, 70·8. Calc. : C, 26·6 ; H, 2·7 ; Br, 70·8%), was obtained which behaved on oxidation as nearly pure *cis*-1 : 4-dibromo-Δ²-*cyclo*hexene (compare Thiele, *loc. cit.*). In view of the evidence furnished by oxidation of the differently derived liquid dibromides, there is every indication that the decomposition which attends the first fractionations is entirely attributable to the presence of the lower-boiling 1 : 2-dibromo-Δ³-*cyclo*hexene, which, on heating, changes into its liquid 1 : 4-isomeride but largely suffers degradation. When the chloroform solution of the bromination product is worked up as described by Thiele, some of the 1 : 2-di-bromide appears to suffer isomerisation in the boiling chloroform and the subsequent decomposition during fractionation is lessened.

When the analytically pure liquid obtained by brominating the hydrocarbon in hexane solution was heated at 100° at ordinary pressure, or distilled at reduced pressure, the decomposition was very great. Usually about 45% of the bromide escaped degradation at low pressures, yielding a non-homogeneous liquid, b. p. 65—74°/5 mm.

This liquid on further fractionation yielded pure *cis*-1 : 4-dibromo-*cyclo*hexene, some proportion of which (see below) was present as such at the outset.

Oxidation of trans-1 : 4-*Dibromo-*Δ^2-cyclo*pentene.*—This and the succeeding oxidations of the *cyclo*pentadiene dibromides were conducted in essentially the way already described. In this case the employment of 12·9 g. of the bromide, 120 c.c. of 5% permanganate solution and excess of magnesium sulphate gave a 52% yield of *trans*-1 : 4-dibromo-2 : 3-dihydroxy*cyclo*pentane, m. p. 75° (Found : Br, 61·6. Calc.: Br, 61·5%). This substance, when further oxidised by cold aqueous chromic acid (compare Thiele, *loc. cit.*), gave an 85% yield of *r*-αα′-dibromoglutaric acid, m. p. 142° (Found : Br, 55·3. Calc.: Br, 55·1%).

Oxidation of cis-1 : 4-*Dibromo-*Δ^2-cyclo*pentene.*—The *cis*-bromide (6·8 g.), treated with 83 c.c. of 5% neutral permanganate solution, gave an 80% yield of crude dibromoglycol, which consisted mainly of *cis*-1 : 4-dibromo-2 : 3-dihydroxy*cyclo*pentane, m. p. 76° (mixed m. p. with the corresponding *trans*-glycol, 45—50°), but contained a quantity of syrupy glycol, presumably the isomeric 1 : 2-dibromo-compound. The former substance on further oxidation by Thiele's method gave *meso*-αα′-dibromoglutaric acid, m. p. 170° (Found : Br, 55·5. Calc.: Br, 55·1%). The crude glycol when similarly oxidised gave this acid contaminated with a syrupy bromo-acid. Both dibromoglutaric acids yielded glutaric acid when reduced with zinc and acetic acid as recorded by Thiele.

Oxidation of 1 : 2-*Dibromo-*Δ^3-cyclo*pentene.*—The liquid dibromide (24·8 g.) obtained by brominating *cyclo*pentadiene in hexane, when treated with 5% neutral permanganate solution (23 c.c.), gave a 47% yield of a water-soluble, non-solidifiable, syrupy glycol. This substance, from which none of the isomeric dibromoglycols could be separated, decomposed on distillation and could not be further purified. It was further oxidised by aqueous chromic acid, during which (as during oxidation to the glycol stage) much of the material suffered severe degradation. From the syrupy acid so obtained, a very small amount of *meso*-αα′-dibromoglutaric acid was readily separated ; the remainder did not solidify and was directly debrominated with zinc dust and acetic acid. From the product a mixture of glutaconic acid and non-solidifiable acidic material was obtained ; the yield, however, of the former was only small and all attempts to decrease the degradation during oxidation of the 1 : 2-dibromide failed.

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