# LXXIII.—*Properties of Conjugated Compounds. Part VIII. Addition of Bromine to αδ-, αγ-, and βγ-Dimethylbutadienes.*

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THE experiments here described are a continuation of the investigation on the influence of substitution in the butadiene chain on (1) the tendency towards the initial formation of adjacent and terminal dibromides and (2) the related structural mobility of the dibromides themselves. As in previous papers, all methods of determining the constitutions of the bromination products which involve the formation and decomposition of cyclic oxides, interactions with sodiomalonic esters, amines, etc., have been rejected; reliance has been placed on the detailed examination of the action of permanganate and of ozone, and densities and refractive indices have frequently been determined as an aid in detecting isomerisation. The conclusions reached for each hydrocarbon are based on the observations made over a large number of bromination and oxidation experiments.

*αδ-Dimethylbutadiene.*—The addition of bromine to αδ-dimethylbutadiene has been examined by Duden and Lemme (*Ber.*, 1902, **35**, 1338), who obtained their hydrocarbon by the removal of hydrogen bromide from βε-dibromohexane with quinoline. The boiling point of their specimen was somewhat high (87—89°),* but evidence was brought forward which showed that the major portion of the (distilled) dibromide obtained therefrom was the terminal dibromide.

Our experiments have shown that the dibromide produced is a stable compound having no recognisable tendency towards isomerisation at room temperature or on heating. The densities and refractive indices of freshly prepared, distilled, and aged specimens are identical, and the evidence of oxidation processes indicates the absence therefrom of any proportion of an isomeride. Consequently the formation of a homogeneous terminal dibromide from this hydrocarbon appears to be more complete than in any instance yet investigated. In order to show this directly, attempts have been made to convert the dibromide quantitatively into its dihydroxy-derivative, CHMeBr·CH(OH)·CH(OH)·CHMeBr, a solid form of which (see p. 516) is readily produced during oxidation with permanganate. Invariably, however, two dibromoglycols are formed—the solid already mentioned (representing about 60% of the dibromide which suffers oxidation) and a liquid which loses hydrogen bromide during distillation. The former resists the further action of cold permanganate, but the latter is so readily attacked that its degradation proceeds side by side with the preliminary hydroxylation of the hydrocarbon dibromide. Consequently the liquid dibromoglycol is always accompanied by considerable quantities of α-bromopropionic, lactic, and pyruvic acids : presumably these are its own degradation products, but since it is obtainable only in small yield, a direct demonstration of its oxidisability to these substances has not been possible.

*αγ-Dimethylbutadiene.*—The hydrocarbon was obtained by dehydration of β-methylpentane-βδ-diol, $OH\cdot CMe_2\cdot CH_2\cdot CHMe\cdot OH$, the reduction product of diacetone alcohol. Our early experiments on the oxidation of the derived dibromide at once showed that the constitution of αα-dimethylbutadiene assigned to the hydrocarbon by Kyriakides (*J. Amer. Chem. Soc.*, 1914, **36**, 994) was incorrect,

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* The homogeneity of conjugated hydrocarbons prepared by recorded methods has been concurrently investigated by one of us with Dr. F. L. Warren. The results of this investigation will shortly be published together with the physical properties of the seven mono- and di-methylbutadienes. For this reason, physical data (other than boiling points) relating to hydrocarbons are here omitted. For convenience in this and subsequent papers, the Geneva names for the hydrocarbons are restricted to the experimental portion.

but details of the establishment of the alternative constitution are here omitted because Diels and Alder (*Annalen*, 1929, **470**, 98) have shown that this and several other methods believed to give the αα-hydrocarbon yield in fact the αγ-isomeride. The intermediate dehydration product, represented as $CMe_2{:}CH{\cdot}CHMe{\cdot}OH$ by Kyriakides, is probably an isomeric methylpentenol, since we could not isolate acetone from its oxidation products.

The oily dibromide obtained from αγ-dimethylbutadiene is unstable, suffering partial degradation to a monobromide on heating or (slowly) on standing. Since at *each* successive distillation a considerable portion of the dibromide is broken down, leaving a residue which is to all appearances homogeneous and without tendency towards isomeric change, there is nothing to suggest that a preferential degradation of one component in a mixture of αβ- (or γδ-) and αδ-dibromides is taking place. The densities of freshly prepared undistilled and distilled samples do indeed differ slightly (1·586 and 1·603 respectively), probably owing to the formation of a trace of monobromide during the isolation of the former. Permanganate oxidation experiments with distilled and undistilled specimens of the dibromide show that *at least* it consists largely of the terminally dibrominated compound $CHMeBr{\cdot}CH{:}CMe{\cdot}CH_2Br$, and both permanganate and ozone oxidations fail to furnish any vestige of positive evidence pointing to the initial occurrence of a proportion of an αβ- or γδ-isomeride. Although ozonolysis might be expected to reveal the presence of any appreciable proportion of either of these forms, the difficulties attending the examination of the products of permanganate oxidation and of ozonolysis are such that small quantities of their degradation products could remain undetected. Permanganate oxidation follows a course similar to that outlined in the preceding section, and therefore quantitative conversion into stereoisomeric dibromoglycols is not possible.

*βγ-Dimethylbutadiene.*—The bromination of βγ-dimethylbutadiene has been extensively investigated (Mariuza, *J. Russ. Phys. Chem. Soc.*, 1889, **21**, 434; Couturier, *Ann. Chim.*, 1892, **26**, 480; Kondakov, *J. pr. Chem.*, 1900, **62**, 166; Courtot, *Bull. Soc. chim.*, 1906, **35**, 969). The completion of our study of this process synchronised with the publication of further work on the subject by Macallum and Whitby (*Trans. Roy. Soc. Canada*, 1928, III, **22**, 33), to whom we are indebted for an early copy of their memoir.

βγ-Dimethylbutadiene, when brominated at a low temperature, readily yields a mixture of dibromides. The main constituent is a solid terminal dibromide, $CH_2Br{\cdot}CMe{:}CMe{\cdot}CH_2Br$, m. p. 47° (Kondakov, *loc. cit.*; Macallum and Whitby, *loc. cit.*; p. 520 below), but the nature of the residual liquid product has not been determined.

Assuming that the liquid, like the solid, is an $\alpha\delta$-compound, Macallum and Whitby attempted to determine which is the *cis*- and which the *trans*-form by causing reaction with diethylamine. The results were anomalous and the authors state that the explanation may be that the liquid dibromide is a mixture rather than a chemical individual.

The liquid dibromide cannot be freed from the dissolved solid form by repeated freezing and filtration (with or without a solvent); the freezing point of the residual liquid, however, rises considerably and the density diminishes. A close estimate of the composition of the dibromide mixture has consequently not been possible. The solid form is certainly produced originally to the extent of more than 80% of the total yield, and it gives, on heating at 100°, a liquid which is *in no respect distinguishable* (this applies to general properties and behaviour on oxidation and distillation) from that obtained by direct bromination. This liquid, after being freed as far as possible from the solid form, represents about 18% of the bromide taken. The reverse change, liquid ⟶ solid, can be brought about by heating for a short time at 100°; we have not thus succeeded in obtaining so high a yield as 80% of the solid form, but estimation has been difficult with the comparatively small quantities of purified material available. The use of quinoline perbromide as a brominating agent causes a considerable diminution in the proportion of solid bromide separable from the product but offers practical difficulties in large-scale preparations.

Macallum and Whitby state that both liquid and solid dibromides distil at 105—110°/18·5 mm. We have found, by repeated tests with the " frozen out " liquid, that distillation begins at 101° and continues to 105° at 15 mm. (the solid distils at 103—105° with some change to the liquid form); the character of the fractions collected over 1° ranges indicates that the solid form (already present or formed during distillation) progressively volatilises in the vapour of the liquid form. Nevertheless, the difference in boiling point of the two substances is much smaller than that of the corresponding butadiene derivatives.

Long-continued degradation experiments have failed to demonstrate that the liquid form is the $\alpha\beta$-dibromide. In all our oxidations, as was to be expected, degradation products from the solid dibromide appeared. Otherwise the products from the two dibromides differed considerably. Ozonolysis of $\alpha\beta$-hydrocarbon dibromides has rarely been satisfactory in our hands; gross decomposition, involving loss of hydrogen bromide, usually occurs during hydrolysis of the ozonide, and, in this instance, although the presence of formaldehyde and of a bromo-ketone other than bromoacetone could be detected amongst the non-resinous products, the expected ketone $CH_3{\cdot}CO{\cdot}CMeBr{\cdot}CH_2Br$ (or its debromination product, methyl *iso*propenyl ketone) could not be recognised. Nevertheless, in view of the fact that ozonolysis of the solid dibromide readily gives bromoacetone in more than 80% of the theoretical yield, the difference in behaviour of the two isomerides on oxidation is hardly to be reconciled with a differentiation of merely *cis-trans*-nature. There remains for consideration the possibility that the liquid portion of the bromination product is a mixture of two liquid dibromides, namely, the αβ- and the *cis*-αδ-compound. No adequate ground for considering this to be the case has been encountered, yet statements or suggestions to the effect that the *cis*-αδ-dibromide is the principal constituent of the bromination product are exceedingly difficult to prove or disprove : it is very doubtful if any constitutional significance is to be attached to the double decomposition reactions (Braun, *Ber.*, 1922, **55**, 3536; Macallum and Whitby, *loc. cit.*) of substances so mobile as those under consideration.

In this series of papers, the addition of bromine to hexatriene, butadiene, *cyclo*pentadiene, *cyclo*hexadiene, and three of the five dimethylbutadienes has been discussed. Amongst these instances the isomerising capacity of dibromide forms is widespread : yet with fair certainty in the case of αδ-dimethylbutadiene and with a high degree of probability in the case of αγ-dimethylbutadiene it has been shown that the bromination product is entirely non-mobile; moreover, in neither of the latter instances has it been possible in a large number of experiments (free bromine being the addendum) to alter recognisably the composition of the bromination mixture. It seems unlikely, therefore, that experimental conditions leading to the production of only αβ- (γδ-) forms could be obtained in these instances, and, that being so, the *general* possibility in this direction disappears. Of the hydrocarbons mentioned above, only *cyclo*hexadiene (J., 1929, 172) has been considered to suffer complete αβ-dibromination, and in determining the orientation of its dibromides importance has been attached to the great contrast between the oxidisability and extent of degradation of the dibromoglycols from original and from derived forms. It is now clear that there is quite a considerable, although less marked, difference in oxidisability of the isomeric dibromoglycols from αδ-forms (the carbon atoms carrying bromine are not here, however, oxidised to carboxyl) and to this extent the evidence formerly relied on is weakened. An attempt is being made to improve the oxidative technique employed in the degradation of dibromoglycols, and it is hoped later to supplement the evidence already brought forward in connexion with the constitution of the *cyclo*hexadiene addition products.

## EXPERIMENTAL.

αδ-Dimethylbutadiene ($\Delta^{\beta\delta}$-hexadiene) was prepared by the catalytic dehydration of ethylpropenylcarbinol (Kyriakides, *J. Amer. Chem. Soc.*, 1914, **36**, 994). The hydrocarbon, after being thoroughly washed and dried, was fractionated over sodium, the portion of b. p. 80—82° being used. This preparation gave a quantitative yield of 3 : 6-dimethyl-$\Delta^4$-tetrahydrophthalic anhydride, m. p. 92°, with maleic anhydride (Found : C, 66·7; H, 6·65. Calc. for $C_{10}H_{12}O_3$ : C, 66·7; H, 6·7%). Diels and Alder (*loc. cit.*, p. 102) give the m. p. as 95—96°.

*Bromination.* This was carried out under conditions similar to those previously described (Farmer and Scott, J., 1929, 172). The dibromination product, after removal of the solvent (both hexane and chloroform were used), was an almost colourless oil (Found : Br, 65·8. $C_6H_{10}Br_2$ requires Br, 66·1%). It had $d_4^{19^\circ}$ 1·621 and $n_D^{19^\circ}$ 1·536 immediately after isolation, and almost the same values after it had been (*a*) slowly distilled or (*b*) kept at room temperature for several days. On distillation the crude dibromide in the different preparations yielded only insignificant quantities of low-boiling material. The distillate was always a colourless oil (b. p. 85°/11 mm., $d_4^{19^\circ}$ 1·622, $n_D^{19^\circ}$ 1·534. Found : Br, 66·2%) which appeared to be homogeneous (Duden and Lemme, *loc. cit.*, also give b. p. 85°/11 mm.). Distilled and undistilled specimens of the substance were repeatedly submitted to oxidation with permanganate and with ozone (see below) in order to detect admixed isomeric dibromides, if such were present. The failure to find even small amounts of the degradation products of the latter, and the complete absence of any detectable tendency to partial isomerisation as revealed by changing physical constants, point to the fact that the addition product is pure βε-*dibromo*-$\Delta^\gamma$-*hexene*.

Unless the bromination was carried out in very dilute solution, there was a tendency towards the production of tetrabromides.

*Oxidation of* βε-*Dibromo*-$\Delta^\gamma$-*hexene*.—The oxidation with neutral permanganate at 0° was carried out essentially as previously described (Farmer and Scott, J., 1929, 172). Since no difference could be detected between the oxidation products of distilled and of undistilled specimens of the dibromide, only typical experiments are here included. In these, 20 g. portions of the dibromide, dissolved in acetone, were supplied with (*a*) 1 atom and (*b*) 4 atoms of oxygen per molecule.

(*a*) On removal of the acetone from the filtered oxidation liquor in a current of air, a semi-solid mixture separated containing unchanged dibromide. This was combined with a small residue from the acetone washings of the manganese mud. The solid portion of the mixture was removed, and the filtrate thoroughly extracted with water; the residue was unchanged dibromide. The aqueous liquor, together with the cold aqueous extract of the manganese mud, yielded, on extraction with pure ether, a syrup from which crystals of the solid material separated. This solid, which crystallised from petroleum in colourless prisms, m. p. 95°, was *βε-dibromohexane-γδ-diol* and was doubtless identical with the dibromohexanediol of Duden and Lemme, for which no m. p. is recorded (Found : Br, 58·0. $C_6H_{12}O_2Br_2$ requires Br, 58·0%). On further oxidation with permanganate it was converted into α-bromopropionic acid, mixed with some lactic acid, and finally into pyruvic acid (phenylhydrazone, m. p. 191°; mixed m. p. with authentic specimen, 191°); with aqueous chromic acid it gave a 75% yield of crystalline α-bromopropionic acid (Found : Br, 52·4; equiv., 153. Calc. : Br, 52·3%; equiv., 153).

The water-soluble syrup accompanying the solid dibromohexanediol, when freed as thoroughly as possible from the latter, amounted to 5—10% of the total oxidation products isolated. Although it differed considerably from the solid dibromoglycol in its greatly inferior stability towards permanganate and towards heat, it appeared to be a stereoisomeride (or mixture of stereoisomerides) of βε-dibromohexane-γδ-diol (Found : Br, 58·4%). When it was heated under reduced pressure, decomposition took place, giving dehydrobromination products which appeared to be partly of cyclic-oxide and partly of ethylenic type (the main portion, b. p. 115—125°/1 mm., corresponded closely in bromine content to the formula $C_6H_{11}O_2Br$); the highest fraction (about 1/3 of the whole), however, consisted of the solid dibromoglycol, which appeared to have been formed by isomerisation during heating. The liquid dibromoglycol was obtained in reasonably pure condition only at a late stage in the experiments and the amount of material accumulated was insufficient for making trustworthy observations as to its oxidation products. The aqueous liquors, when acidified and extracted with ether, yielded a small quantity of acidic liquid. This was fractionated and consisted mainly of α-bromopropionic acid; pyruvic acid was present in the very small, low-boiling fraction.

(*b*) In effecting more complete oxidation of distilled and of undistilled specimens of the dibromide it was desired to search for αβ-dibromobutyric and α-bromocrotonic acids, the acidic fission products of an αβ-dibromide (acetic acid, the complementary fission product, if detected, could have arisen from the acetone used as solvent). The acid product, when carefully fractionated, was found to consist mainly of α-bromopropionic acid, mixed with lactic acid and a little pyruvic acid—this mixture gave excellent yields of pyruvic acid on further oxidation—but αβ-dibromobutyric or α-bromocrotonic acid could not be found.

The absence of any significant quantity of an αβ-dibromide followed, however, more convincingly from the result of parallel ozonisation experiments. In all these experiments the decomposition of the ozonide by water was carried out at the lowest effective temperature while carbon dioxide was passed through the apparatus to sweep out any acetaldehyde or other volatile product that might have been formed. Immediately the decomposition was complete the cold aqueous reaction product was treated with 30% hydrogen peroxide and kept for 12 hours (isolation of the brominated products as aldehydes was not possible owing to their facile polymerisation). In no experiment could a trace of acetaldehyde, or indeed any highly volatile product, be detected; similarly, none of the degradation products to be expected from an αβ-dibromide could be separated or derived from the acidic reaction product.

*αγ-Dimethylbutadiene* (*δ-Methyl-$\Delta^{\beta\delta}$-pentadiene*).—The hydrocarbon (see p. 511), after being thoroughly washed with water and fractionated over sodium, boiled at 75·8—76·0°. It gave a quantitative yield of the maleic anhydride addition compound.

*Bromination.* Both hexane and chloroform were used as solvents during bromine addition, but no difference could be detected in the products. The undistilled dibromide, $d_{4^\circ}^{20\cdot5^\circ}$ 1·624, was an almost colourless oil (Found: Br, 66·1. $C_6H_{10}Br_2$ requires Br, 66·1%).

On distillation the dibromide decomposed to an extent which varied in different experiments. Fractions were collected, as shown below, some carbonised residue always remaining in the flask.

| B. p. at 22 mm. | Proportion (%). | Bromine content (%). |
|---|---|---|
| 70— 86° | 3— 7 | 52·8 |
| 86— 96 | 6—11 | 61·2 |
| 96—104 | 50—80 | 66·0 |
| 104—115 | 10—15 | — |

The bromine content showed that, although more than half the distilled material consisted of dibromide, a considerable portion had lost hydrogen bromide. At each subsequent redistillation of the dibromide fraction (b. p. 101—103°/22 mm.) a partly carbonised residue and a low-boiling fraction (below 80°/22 mm.) were again obtained, the yield of the latter depending to some extent on the rate of distillation. Redistillation of the low-boiling portions yielded a colourless oil, b. p. 60—62°/22 mm., which was apparently an almost pure bromo-αδ-dimethylbutadiene (Found: Br, 51·1.

$C_6H_9Br$ requires Br, 49·6%). As a result of the observations here recorded, the original dibromination product is regarded as pure or only slightly impure *βε-dibromo-δ-methyl-$\Delta^\delta$-pentene.*

*Oxidation of* *βε-Dibromo-δ-methyl-$\Delta^\delta$-pentene.*—Here also, repeated experiments disclosed no constitutional difference between freshly prepared, undistilled specimens, and the dibromide fraction of b. p. 101—103°/22 mm.; accordingly, in the following account of oxidation by (*a*) ozone and (*b*) neutral permanganate, the nature of the specimen is not indicated.

(*a*) The dibromide, dissolved in chloroform, was submitted to ozonisation for 24 hours. The crude ozonide obtained on removal of the chloroform was decomposed by gentle warming with water and the decomposition products were extracted with pure ether. The extract was washed with sodium bicarbonate solution, and the ether removed. The residue on distillation yielded the fractions (i) b. p. 50—60°, (ii) b. p. 60—95°, and (iii) b. p. 95—115° at 22 mm. Of these, the first consisted almost wholly of bromoacetone (Found : Br, 56·2. Calc. for $C_3H_5OBr$ : Br, 58·4%. Semicarbazone, m. p. 143°; mixed m. p. with authentic specimen, 143°) and the last consisted partly of unchanged dibromide. As α-bromopropaldehyde, the fission product complementary to bromoacetone, is destroyed by distillation, it was necessary to isolate it as the corresponding acid. Accordingly in another experiment the aqueous liquor containing the decomposed ozonide was allowed to stand with hydrogen peroxide. The product, after the neutral material had been removed in ether, was acidified and thoroughly extracted. The dried extract yielded an acidic liquid, from which fractions of b. p. 90—105°/757 mm. (40—100°/22 mm.) and 100—120°/22 mm. were obtained; the former satisfied no test for formic acid or acetic acid, and the latter, consisting of somewhat impure bromopropionic acid, was readily converted successively into sodium lactate and pyruvic acid (phenylhydrazone, m. p. 191°; mixed m. p. with an authentic specimen, 191°). It was thus established that both fission products of an αδ-dibromide were produced in considerable amounts; it remained to search for fission products of an αβ- and of a γδ-dibromide. Since little success attended the manipulation or attempted isolation of the non-volatile brominated aldehydes and the acids derived therefrom by gentle oxidation, effort was especially directed to the recognition of even traces of formaldehyde (from an αβ-dibromide) or of acetaldehyde (from a γδ-dibromide). The vapours generated during the hydrolysis of ozonide specimens were therefore swept by a stream of carbon dioxide into water and into an alcoholic solution of β-naphthol. In the many experiments carried out, the formation of neither formaldehyde nor acetaldehyde could be detected by odour, by the formation of a β-naphthol derivative, or by other tests.

(*b*) The oxidation of the dibromide by neutral permanganate at 0° (1 atom of oxygen per molecule of dibromide) was carried out in acetone solution in the usual way. After removal of the manganese mud and acetone, the aqueous oxidation liquid deposited a solid and an oily liquid. The former was a solid dibromoglycol, which crystallised from petroleum in colourless prisms, m. p. 94—95° (Found: Br, 58·0. $C_6H_{12}O_2Br_2$ requires Br, 58·0%); the latter contained bromoacetone (semicarbazone, m. p. 143°) and unchanged dibromide, both of which were readily separated, but the remaining brominated material decomposed on attempted distillation at 1 mm. pressure. The solid dibromoglycol was βε-*dibromo*-δ-*methylpentane*-γδ-*diol*. When gently oxidised with aqueous chromic acid, it yielded an oil, the neutral portion of which was bromoacetone and the acidic portion was converted into pyruvic acid by hydrolysis and subsequent oxidation with permanganate. Since the solid dibromoglycol was obtained in much smaller yield than the corresponding compound from αδ-dimethylbutadiene, attempts were made to isolate a second isomeric compound. The oxidation products, however, proved too intractable for success in this direction, and attempts to demonstrate by permanganate oxidation anything beyond the fact that a considerable proportion of the dibromide suffered decomposition into the appropriate products proved unprofitable.

βγ-*Dimethylbutadiene*.—The hydrocarbon was prepared from pinacol by the method of Kyriakides (*J. Amer. Chem. Soc.*, 1914, **36**, 987). It was very thoroughly washed, dried, and fractionated; after a final distillation over sodium, it boiled at 69·5—70°/765 mm. Yield, 60%.

*Bromination*. The addition of bromine was carried out in chloroform, carbon disulphide, purified petroleum, ether, and hexane, at —15°. Removal of the solvent under reduced pressure yielded a pale yellow semi-solid mass, from which liquid and solid components were separated by mixing it with light petroleum and freezing out the solid: this was so excessively soluble in the liquid bromide that after six freezings and filtrations only an indifferently good separation was effected. Working without a solvent, or with other solvents, gave even less satisfactory results. The total yield of solid separated was slightly more than 80% of the bromination product. All operations with the bromides were carried out in front of a powerful suction fan on account of their lachrymatory nature.

*The solid portion of the bromination product*. This consisted entirely of the αδ-dibromo-βγ-dimethyl-$\Delta^{\beta}$-butene (colourless needles, m. p. 47°. Found: Br, 66·5. Calc.: Br, 66·4%) described by Kondakov (*loc. cit.*). Concerning its easy and very extensive degradation to bromoacetone by permanganate oxidation and by ozonolysis, our results agreed entirely with those of Kondakov and of Macallum and Whitby (*loc. cit.*).

When heated at 100° for 1 hour, the solid dibromide suffered partial conversion into a liquid. This liquid, freed as thoroughly as possible from unchanged solid, amounted to about 18% of the total—a proportion that could not be increased by prolonging the period of heating (decomposition became serious on long heating). It had invariably the correct bromine content and showed no appreciable difference from the directly obtained liquid dibromide when submitted to most of the operations and reactions employed in the examination of the latter. The change produced by heating took place to some extent during distillation, causing the pure substance to boil over a range (103—105°/15 mm.); the distillate yielded a small proportion of oily dibromide.

*The liquid portion of the bromination product.* When strongly cooled, the liquid product solidified to a hard crystalline mass; this rapidly liquefied when the temperature rose, leaving crystals of the solid form temporarily undissolved. It distilled completely between 101° and 105° at 15 mm., the fractions collected at 1° intervals freezing with different degrees of ease. Attempts were made, by distilling a considerable quantity of the liquid dibromide, to isolate a pure compound, but none of the fractions appeared to be free from the solid dibromide: indeed, distillation gave no better separation than filtration and resulted in considerable loss of liquid material by isomerisation. Such isomerisation was readily effected by heating the liquid compound at 100° for a few minutes; after dilution and cooling, the solid compound could be filtered off.

*Ozonolysis of the Liquid Bromination Product.*—The liquid, dissolved in chloroform and cooled in an ice–salt mixture, was ozonised for 8 hours. The ozonide decomposed very slowly when gently heated with water, giving a large quantity of resinous material. The aqueous liquor, in which formaldehyde could be detected, was submitted to steam distillation; the volatile degradation products were extracted with ether and fractionated. The distillate comprised (i) bromoacetone, b. p. 45—50°/16 mm. (semicarbazone, m. p. 143°; Found: Br, 58·6. Calc.: Br, 58·4%); (ii) a bromine-containing mobile liquid, b. p. 50—55°/16 mm., which yielded a crystalline precipitate with semicarbazide, the precipitate being halogen-free and giving a red colour with ferric chloride; (iii) a small amount of a mobile bromine-containing liquid, b. p. 55—90°/16 mm.; and (iv) a viscous high-boiling fraction which contained some unchanged dibromide but consisted mainly of polymerised material.

The liquid produced by heating the solid dibromide gave exactly similar products, but in neither case was it possible to isolate pure substances directly or indirectly from the distillate.

*Permanganate Oxidation of the Liquid Bromination Product.*—The bromine, in 15—20 g. portions, was suspended in water (or dissolved in acetone) and oxidised with neutral permanganate at 0° (1 atom of oxygen per molecule). The product, worked up in the usual way and freed from traces of acidic matter, was a liquid which yielded on distillation the fractions: (i) bromoacetone, b. p. 45—50°/15 mm.; (ii) and (iii) mobile bromine-containing liquids (partly at least ketonic) similar to the corresponding fractions of the ozonolysis product; (iv) a mobile liquid, b. p. 93°/16 mm., obtained in considerable yield and evidently derived from a dibromoglycol by loss of hydrogen bromide (Found: C, 35·5; H, 5·8; Br, 40·4. $C_6H_{11}O_2Br$ requires C, 36·9; H, 5·6; Br, 41·0%); (v) a viscous liquid, b. p. 120°/16 mm., apparently derived from a dibromoglycol by loss of hydrogen bromide (Found: C, 33·2; H, 4·9; Br, 45·4%); (vi) a small quantity of a solid dibromoglycol, b. p. 148°/16 mm., which crystallised from petroleum in colourless prisms, m. p. 93° (Found: Br, 57·5. $C_6H_{12}O_2Br_2$ requires Br, 57·2%). Since this was further oxidisable to bromoacetone, it was *αδ-dibromo-βγ-dihydroxy-βγ-dimethylbutane.* The liquid obtained by heating the solid dibromide yielded similar oxidation products.

For comparison, the solid dibromide was likewise oxidised with permanganate, only 1 atom of oxygen per molecule being used. There were obtained: (i) bromoacetone; (ii) a small amount of viscous liquid, b. p. about 120°/15 mm., which from its nature and composition appeared to be somewhat impure dibromoglycol; (iii) a large amount of the solid dibromoglycol, m. p. 93°, described above. Thus, whereas the solid dibromide yielded two dibromoglycols and some bromoacetone, the liquid yielded (in addition to a minor proportion of the same products) a very considerable proportion of other products, including dihydroxylated compounds which had lost hydrogen bromide. The difference between the oxidation products of the two dibromides was maintained from experiment to experiment; but since permanganate oxidation appeared quite unlikely to furnish conclusive evidence of the constitution of the liquid dibromide, experiments were discontinued.

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