CCCLXXXII.—*The Modes of Addition to Conjugated Unsaturated Systems. Part III. Further Remarks and Observations bearing on the Mechanism of Addition of Halogens and Hydrogen Halides.*

By Christopher Kelk Ingold and Henry Geoffrey Smith.

(1) *Additions of Halogens to Conjugated Unsaturated Systems in which Structural Influences favour Anionotropic Change* (Case 1a; compare J., 1928, 910).

Orientation.—The addition of halogens to conjugated unsaturated hydrocarbons was discussed in Part I (*loc. cit.*; compare J., 1929, 2022, footnote), where it was shown that the views advanced regarding these reactions accommodated all the relevant facts up to then established. In order to provide further illustrations of the method of applying the theory several predictions were made, and one of these, namely, that the dibromide of βγ-dimethylbutadiene should contain a high proportion of the 1 : 4-isomeride, previous conclusions to the contrary notwithstanding, has since been verified (Farmer, Lawrence, and Scott, J., 1930, 510). Farmer and his collaborators have also shown (*loc. cit.*; J., 1929, 172) that high proportions of 1 : 4-product are obtained from αδ- and αγ-dimethylbutadiene,* and that the proportion of the 1 : 4-dibromide of *cyclo*pentadiene is increased when the solvent is changed from hexane to chloroform. All these results, published subsequently to the appearance of Part I, are consistent with the theory and are implicit as predictions in the discussion. Consistent, although less crucial, is Muskat and Northrup's recent observation (*J. Amer. Chem. Soc.*, 1930, **52**, 4043) that the addition of chlorine to butadiene yields both 1 : 2- and 1 : 4-products. The considerations relating to the above methylated butadienes follow directly from the analogous illustrations which were given, and it was shown to be a general consequence of the theory that the proportion of 1 : 2-compound formed in a non-polar or difficultly polarisable solvent should be higher than that produced in a polar or readily polarisable solvent. Amongst the applications of theory given in Part I are several which illustrate the effects to be anticipated from the presence of ethenyl and aryl substituents, and it is explained, *inter alia*, why α-phenylbutadiene should yield practically exclusively γδ-dihalides. Muskat and Huggins subsequently showed (*J. Amer. Chem. Soc.*, 1929, **51**, 2496) that the dichloride, prepared in various solvents at widely differing temperatures, uniformly possesses this orientation.

Thus, so far as orientation in the addition of halogens to conjugated unsaturated hydrocarbons is concerned, the theory has hitherto remained consistent with established results. Two further developments seem desirable.

The first relates to the provision of typical instances of oriented halogen additions outside the range of additions to aliphatic and aromatic hydrocarbons. Besides alkyl, ethenyl and aryl substituents, any suitably placed, neutral group, containing unshared electrons in association with the atom by which it is attached, must fall within the category of influences favourable to anionotropic change, and must therefore come into the purview of constitutional effects indicated in the heading to this section. Methoxyl- and halogen-substituted, conjugated poly-enes should therefore fit into the theoretical scheme hitherto illustrated exclusively by reference to the reactions of hydrocarbons : α-bromobutadiene should add in the γδ-positions, α-bromohexatriene in the εζ-positions, *p*-bromo-αδ-diphenylbutadiene in the γδ-positions, and so on. No data

---

* The former result is confirmation of a previous finding by Duden and Lemme (*Ber.*, 1902, **35**, 1388) with which the authors of Part I were unacquainted.

concerning examples of this type appear to have been recorded hitherto, and we have therefore examined the action of bromine, in hexane, in chloroform and in acetic acid, at various temperatures, on α-bromobutadiene. We are able to show that in all cases the dibromide has the expected orientation and is unaccompanied by any perceptible amount of an isomeride.

Incidence of Reaction.—The second development concerns the provision of a more intimate test of mechanism than is likely to be furnished by the accumulation of further orientation results of the type considered above.

The theory of halogen additions presumes initial attack by the halogen molecule at the α-atom of the butadiene chain, leading to the entrance of a halogen kation at this point, subsequent distribution of the remainder of the halogen molecule between the β- and δ-carbon atoms depending on a transient electrolytic dissociation and a contemporaneous electromeric change identical in type with that which characterises ordinary anionotropic systems. Now prior attack at the α-carbon atoms is a necessary supposition so far as the formation of the 1 : 4-compound is concerned, but there is a possible alternative conception of the source of the 1 : 2-isomeride, namely, that attack commences at the β-carbon atom; for it is evident that a reaction thus initiated could be completed only by the attachment of the halide residue to the α-atom of the system.* Thus, in contrast to our view † which makes differences of orientation dependent on differences in the mode of completion of reaction, it would be possible to attempt to relate orientation phenomena to differences in reaction incidence. The diagnosis of an unsymmetrical halide such as a 1 : 2-dibromide does not, of course, in itself yield any information about the order of the entrance of the halogen atoms, and thus it seemed desirable to determine, for some typical unsymmetrical addition products, which is the point of initiation of addition and which the point of its completion.

Two methods were employed for this purpose. In the first, which was applied to butadiene, the addition of iodine monochloride was studied. The fundamental assumption is that the location of the

---

* The conditions of addition here contemplated are such as would preclude a substantial amount of anionotropic interconversion of the fully formed isomerides, and it is known that these conditions are normally realised in the addition of bromine to butadiene (Farmer, Lawrence, and Thorpe, J., 1928, 729).

† This does not arbitrarily and completely exclude β-attack; but each vinyl group of the butadiene chain is a powerful electron-source, wherefore the α-positions should be activated and α-attack should prevail. Our attitude with regard to the assumption of simultaneous β-attack is, therefore, that it must await the provision of evidence requiring it.

iodine atom in the addition product marks the point of commencement of the reaction (Ingold and Smith, this vol., p. 2742). Farmer, Lawrence, and Thorpe found (*loc. cit.*) that the product of the addition of two atoms of bromine to butadiene in chloroform at − 15° contained, besides the preponderating 1 : 4-dibromide, some 37% of the 1 : 2-compound. We find that in the product of the action of iodine monochloride on butadiene in methylene chloride at − 35° the 1 : 4-addition compound, $CH_2I{\cdot}CH{:}CH{\cdot}CH_2Cl$, which here also is the main constituent, is accompanied by not less than 22% of the 1 : 2-isomeride. $CH_2I{\cdot}CHCl{\cdot}CH{:}CH_2$; we have no evidence that the other possible product of 1 : 2-addition, $CH_2Cl{\cdot}CHI{\cdot}CH{:}CH_2$, was present in significant quantity. The two dihalogeno-compounds, on elimination of hydrogen halide, yielded α- and β-chlorobutadiene respectively,* and these, on addition of bromine,† gave the appropriate chlorodibromobutenes, from which the expected products were derived by ozonolysis. The constitutions thus established for the two chloroiodo-compounds both indicate the C_{α}-atom as the point of incidence of reaction, and the obvious analogies with the addition of bromine show that the theory of C_{α}-initiation is adequate to account for the formation of both dibromides.

We did not employ an analogous method in the case of isoprene because certain of its possible addition compounds would be tertiary halides, and the marked tendency to ionise possessed by tertiary halogen would have introduced complications. For instance, anionotropic systems in which the mobile group is a tertiary halogen atom are known to be exceptionally labile and the occurrence of isomerisation subsequently to the completion of addition would accordingly have been difficult to prevent. In order to avoid this disturbance we made use of the competition principle established by the experiments of Terry and Eichelberger (*J. Amer. Chem. Soc.*, 1925, **47**, 1067) and of Francis (*ibid.*, p. 2340). These authors have shown (compare Burton and Ingold, J., 1928, 912; Ingold, *Ann. Reports*, 1928, **25**, 131) that the kation, $CH_2Br{\cdot}CH_2^{\oplus}$, formed in the first stage of the addition of bromine to ethylene can be caused to take up a foreign anion in place of the originally liberated bromide ion. The foreign ion will naturally compete with a success proportional to its aptitude for co-ordination and to its concentration; accordingly, whilst a stable anion, with small power of co-ordination,

---

* The degradation of β-phenylethylammonium hydroxides (Hanhart and Ingold, J., 1927, 997), in which the −*T*-effect is exerted by phenyl in the presence of a proton-seeking reagent, provides analogy for the expected effect of vinyl in these reactions.

† This takes place at the double linking which is least de-activated by the halogen originally present (Ingold and Ingold, J., 1930, 2354).

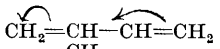
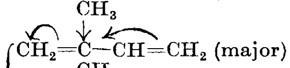
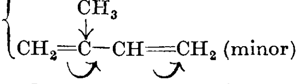
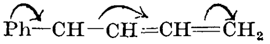
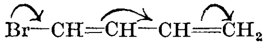
e.g., NO_3', is best introduced in large concentration as a soluble salt, *e.g.*, $NaNO_3$, an unstable anion, having a large tendency to co-ordinate, *e.g.*, OH', may be supplied as the anionic component of a feebly ionising, covalent substance, such as water :

$$CH_2{:}CH_2 \xrightarrow{Br_2} CH_2Br{\cdot}CH_2^{\bullet} + Br' \xrightarrow{H_2O} CH_2Br{\cdot}CH_2{\cdot}OH + Br' + H^{\bullet}.$$

It is clear that this process can be applied in the study of the modes of addition of conjugated unsaturated systems, and that, having a choice of competing anions, it should be possible to select one which would not migrate subsequently to the completion of addition. In order to ensure the requisite inertia in the anionotropic systems which might be formed by addition, all that is necessary is that the anion shall be sufficiently basic (Burton and Ingold, J., 1928, 904); and to this end we chose the hydroxide ion as a competing anion suitable for the intended application to isoprene, and introduced it, in the form of water. From the theory of the process it is evident that the location of the hydroxide ion (as a hydroxyl group) in the final product will indicate the point of completion of the reaction, and will thus yield indirect evidence as to its point of incidence. Staudinger, Muntygler, and Kupfer have shown (*Helv. Chim. Acta*, 1922, **5**, 756) that the product of the addition of two atoms of bromine to isoprene consists largely of the 1 : 4-dibromide, but the presence of comparatively small amounts of 1 : 2-isomerides would not have been detected by their method. Bromination in the presence of water under our conditions led to a mixture of several bromo-hydroxy-compounds. The principal product (at least 47%) had the constitution $CH_2Br{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}OH$. This substance obviously corresponds to the 1 : 4-dibromide recognised as the main isomeride by Staudinger and his collaborators, and the constitution of the hydroxy-compound shows that, in the formation of these products of terminal addition, reaction commences preferentially at the C_α-end of the β-methylbutadiene chain; and C_α-attack corresponds to polarisation in that direction, which would be favoured by the inductive electron repulsion of the β-methyl substituent. An important by-product (at least 16%) had the structure $CH_2Br{\cdot}CMe(OH){\cdot}CH{:}CH_2$. Although this is a 1 : 2-addition compound, its constitution proves that it also arises from a reaction initiated at the α-carbon atom ; this substance also results, therefore, from a normal primary polarisation. In addition to these two compounds a third isomeride (small amount), of the formula $CH_2(OH){\cdot}CMe{:}CH{\cdot}CH_2Br$, was qualitatively recognised. Since an anionotropic modification of this substance would be a tertiary bromide, the established structure, whilst indicating C_δ-attack, does not directly exclude the theory of C_β-initiation; nevertheless we have encountered no evidence either of C_γ-attack in isoprene or of C_β-attack in butadiene, both modes of reaction which are intrinsically more probable than C_β-attack in isoprene, and on these indirect grounds we are disposed to accept at its face-value the evidence furnished by the constitution of the compound that it arises from a reaction incident at the δ-carbon atom. Whether this deduction is correct or not, the structure clearly establishes the occurrence of a small amount of polarisation in the direction contrary to that favoured by the polarity of the β-methyl substituent. The method employed to determine the constitutions of these bromo-hydroxy-compounds was in all cases the same, namely, removal of the halogen atom by reduction and subsequent ozonolytic fission.

Finally the action of bromine on α-phenylbutadiene was also examined under analogous conditions of competition. After removal of the bromine atom the hydroxyl group was located on the γ-carbon atom, and this shows the bromohydrin to have the constitution $CHPh{:}CH{\cdot}CH(OH){\cdot}CH_2Br$. Accordingly it must be concluded that the addition of the halogen is initiated at the δ-carbon atom; and this is the anticipated position, because the strong electron-releasing capacity of the phenyl substituent would induce polarisation in the corresponding direction.

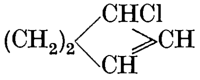
Our conclusions in relation to the modes of polarisation of the conjugated unsaturated compounds studied in their additive reactions with halogens, and with regard to the orientations of the points of incidence of reaction and the orientations of the products, may be summarised as follows :

Compound.	Polarisation.	Incidence.	Main product.	By product.
Butadiene	 $CH_2{=}CH{-}CH{=}CH_2$	α	αδ	αβ
Isoprene	 $CH_2{=}\overset{CH_3}{C}{-}CH{=}CH_2$ (major)	α	αδ	αβ
	 $CH_2{=}\overset{CH_3}{C}{-}CH{=}CH_2$ (minor)	δ	δα	(?δγ)
α-Phenylbutadiene	 $Ph{-}CH{-}CH{=}CH{=}CH_2$	δ	δγ	—
α-Bromobutadiene	 $Br{-}CH{=}CH{-}CH{=}CH_2$	δ	δγ	—

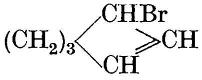
(2) *Additions of Hydrogen Halides to Conjugated Unsaturated Systems in which Structural Influences favour Anionotropic Change* (Case 2a ; compare J., 1928, 910).

The theory of hydrogen halide additions, which are regarded as being initiated by the kationic component of the addendum (Part I, *loc. cit.*; *Ann. Reports*, 1928, **25**, 147; Ingold and Ingold, J., 1930, 2354), follows in a simple manner from the foregoing discussion. The point of incidence of reaction, deduced from the polarity of the substituents as already illustrated, marks the point of entrance of hydrogen. The stable position or positions of the halogen then depend on anionotropic equilibrium (Burton and Ingold, J., 1928, 904, *et seq.*) as affected by the substituents present, including that which has become modified by the accession of the hydrogen atom.

The first of these conclusions is confirmed, without complications related to the second, by the formation of compounds having the properties of allyl halides,



and



from *cyclo*pentadiene and *cyclo*hexadiene respectively (Kraemer and Spilker, *Ber.*, 1896, **29**, 554; Crossley, J., 1904, **85**, 1420): α-attack by the hydrogen of the hydrogen halide is here clearly indicated.

With regard to the second conclusion, it should be noted first that, when hydrogen halide additions to conjugated unsaturated hydrocarbons are carried out, as they frequently are, in a nearly non-polar solvent (*e.g.*, excess of the hydrocarbon), the stable products may not always at once arise if the anionotropic system is insufficiently mobile, *i.e.*, if there is too little tendency towards the dissociation of the ions formed in the first stage of addition. It happens, however, that, in the most thoroughly investigated examples, one of the anionotropes is either a tertiary halide or a benzyl halide and either circumstance would probably confer sufficient mobility on the tautomeric system to permit the expectation of equilibrium products under the experimental conditions recorded. As an illustration reference may be made to Farmer and Marshall's recent demonstration that the monohydrobromide of βγ-dimethylbutadiene (this vol., p. 139), prepared under a variety of conditions, in all cases consists essentially of the product $H\text{CH}_2\cdot\text{CMe}\dot{:}\text{CMe}\cdot\text{CH}_2Br$.

The application of both principles together may be exemplified by the additive reactions of less symmetrically constituted hydrocarbons. Having regard to the normal direction of polarisation of β-methylbutadiene (isoprene) and the structure of the tautomeric kation which would be formed on union with a proton, it will be evident that the main direction of addition of hydrogen bromide should be $\text{H}_\alpha\text{Br}_\delta$. Staudinger, Kreis, and Schilt have in fact shown (*Helv. Chim. Acta*, 1922, **5**, 743) that the main constituent of isoprene monohydrobromide has the constitution $H\text{CH}_2\cdot\text{CMe}\dot{:}\text{CH}\cdot\text{CH}_2Br$. Similarly, the orientation of the addition of hydrogen bromide to α-phenylbutadiene should clearly be $\text{H}_\delta\text{Br}_\gamma$. Riiber has proved

(*Ber.*, 1911, **44**, 2977) that the monohydrobromide of this hydrocarbon has the expected structure, $C_6H_5\cdot CH{:}CH\cdot CH\mathit{Br}\cdot CH_2\mathit{H}$.

Finally, in order to extend the range of experimental illustrations beyond the sphere represented by the addition reactions of hydrocarbons, we have investigated the addition of hydrogen bromide to α-bromobutadiene. The theory of this case is closely similar to that which relates to the corresponding reaction of α-phenylbutadiene, and almost exclusive addition in the sense $H_\delta Br_\gamma$ would be anticipated. We show, in fact, that the homogeneous addition product has the constitution $Br\cdot CH{:}CH\cdot CH\mathit{Br}\cdot CH_2\mathit{H}$.

EXPERIMENTAL.

Action of Iodine Monochloride on Butadiene.—Butadiene was obtained by distilling the liquid deposited by compressed coal gas and also by Thiele's method (*Annalen*, 1899, **308**, 333). The crude hydrocarbon was converted by absorption in bromine into its tetrabromide, m. p. 117°, which was purified by crystallisation from ligroin, and reconverted into butadiene by the action of zinc and alcohol. The gas issuing from this reduction was well scrubbed with water, dried with calcium chloride and phosphoric oxide, and condensed at the temperature of liquid air in a well-dried bulb, from which it was subsequently redistilled (b. p. — 4°).

The iodine monochloride, which was purchased, was purified by distillation under reduced pressure and by partial freezing, precautions being taken against the access of moisture and, as far as possible, of light.

The methylene chloride used as solvent was washed with water, dried with calcium chloride and phosphoric oxide, and distilled.

The halogenation vessel, which was fitted with a mercury-sealed, spiral ribbon stirrer and suitable sealed-in connexions, was dried by warming in a stream of phosphoric oxide-dried air, and was kept in the dark at — 35° in a bath of liquid ammonia throughout the addition experiments.

Methylene chloride was first introduced, then the butadiene was distilled in from a weighed bulb, and finally the correct amount of a dilute solution of freshly purified iodine monochloride in methylene chloride was slowly added with rapid stirring. The light brown oil which remained after the solvent had been pumped off at 0° in the dark in a stream of dry nitrogen at low pressure was digested with an excess of dry, finely divided sodium hydroxide. The vapours which escaped condensation in the short water-cooled condenser were collected in a bulb cooled in liquid air, and the gaseous contents of the apparatus were swept into this bulb with a stream of nitrogen at the end of the decomposition. The same bulb was fitted with an efficient condenser, fed with ice-cold water, to serve as a still-head, and its contents were slowly distilled up to the ordinary temperature, the vapours being led successively through ammoniacal silver nitrate, dilute sulphuric acid, and bromine. The absence of more than a trace of white precipitate in the silver nitrate solution indicated the absence of perceptible quantities of vinylacetylene, and, except in earlier unsuccessful experiments, the recovery of butadiene tetrabromides from the bromine trap was small. The mixture of chlorobutadienes had b. p. 53—63°; yields up to 76% were obtained (Found : C, 53·8, 54·0; H, 5·7, 5·5; Cl, 40·8, 40·6. Calc.: C, 54·2; H, 5·7; Cl, 40·1%).

This mixture was now treated at — 35° in ligroin solution with the calculated amount of bromine, which was added with rapid stirring in exactly the same manner as the iodine chloride in the original addition experiment. The ligroin used was a light fraction which had been purified with fuming sulphuric acid and with permanganate and dried with phosphoric oxide. The bromine employed had been dried with sulphuric acid, distilled, and further purified by partial freezing. After removal of the solvent by distillation through a long Dufton column, the chlorodibromobutenes were obtained as a straw-coloured oil (yields, nearly quantitative) which distilled at 92—96°/15 mm., leaving only a small amount of residue (Found : C, 19·4; H, 2·2. Calc.: C, 19·3; H, 2·0%).

The ozonides, which were obtained from the chlorodibromobutenes by the action of ozonised oxygen in chloroform solution below 0°, were examined in three ways. (1) They were boiled with water for 30 minutes. The volatile products, which were passed through water, yielded carbon monoxide, the identity of which was confirmed by its solubility in ammoniacal copper salts, and an aqueous solution of formaldehyde, the *p*-nitrophenylhydrozone of which was isolated and identified (m. p. and mixed m. p.). The liquid remaining in the flask was made alkaline with sodium hydrogen carbonate, extracted with ether, acidified with mineral acid, and again thoroughly extracted. The neutral extract, which had lachrymatory properties, rapidly developed free hydrogen bromide and yielded a gum, doubtless a polymeric form of α-bromoacraldehyde. The acid extract gave αβ-dibromopropionic acid, which after a single distillation under reduced pressure showed a correct m. p. (62—63°) and mixed m. p. (Found : *M*, by titration, 232. Calc., 232). The aqueous solution remaining from the extractions with ether contained both chloride and bromide, and the weight and composition of the silver salts precipitated from a measured volume indicated the presence of 0·89 mol. of hydrochloric acid and 0·20 mol. of hydrobromic acid per mol. of chlorodibromobutenes. The yield of pure dibromopropionic acid represented 22 mols. % of the original chlorodibromobutenes.

(2) The ozonides were reduced in ethereal solution by the gradual addition of aluminium amalgam until the reactions of ozonides had disappeared. After removal of the residual metal, the acids were extracted with sodium hydrogen carbonate, and the αβ-dibromopropaldehyde obtained on evaporation of the dried ethereal extract was converted by boiling with concentrated aqueous sodium acetate into α-bromoacraldehyde, which was isolated as described below and identified by its odour and lachrymatory character, its b. p. (46°/15 mm.), the m. p. of its semicarbazone (160°), and by analysis (Found : C, 26·9; H, 2·1; Br, 59·5. Calc.: C, 26·7; H, 2·2; Br, 59·3%). The acid recovered from the sodium hydrogen carbonate solution was αβ-dibromopropionic acid, the recovery representing 18 mols. % of the chlorodibromobutenes.

(3) The ozonides were boiled for 15 minutes with a concentrated aqueous solution of sodium acetate, the product was distilled in steam, and the distillate extracted with ether. The extract yielded α-bromoacraldehyde (Found : C, 26·6; H, 2·2%), the yield, allowing for a 60% conversion from αβ-dibromopropaldehyde, corresponding to 58 mols. % of the chlorodibromobutenes.

Action of Bromine and Water on Isoprene.—Isoprene was prepared by thermal decomposition of limonene in Harries and Gottlob's apparatus (*Annalen*, 1911, **383**, 228), which was slightly modified to permit the use of a low pressure as recommended by Staudinger and Klever (*Ber.*, 1911, **44**, 2213). The reflux system included a spiral-coil condenser above the ordinary double-surface condenser, and both units were fed with ice-water; the upper end of the system was connected to a bulb cooled in liquid air and thence to a water-pump. The hydrocarbon fraction of b. p. 30—40° was converted into its hydrobromide by treatment with cold hydrogen bromide in acetic acid (600 g./l.), and the dibromo*iso*pentane, which was separated by precipitation with water and extraction with ether, was carefully purified by distillation (b. p. 74—75°/15 mm.) and decomposed with excess of boiling concentrated methyl-alcoholic potassium hydroxide. In this decomposition a short reflux condenser was used to withhold the alcohol; the isoprene escaped this and was condensed at the temperature of solid carbon dioxide and ether. At the end of the process some water was added to the alkaline solution to facilitate the escape of the hydrocarbon. The recovered isoprene was washed with water, dried with fused calcium chloride, and distilled (b. p. 34°).

Isoprene (20 g.), and a solution of redistilled bromine (15 c.c.) in 50% aqueous alcohol (1 l.), were added alternately in portions of one-fifth, commencing with the isoprene, to the same solvent (2 l.), each addition of isoprene after the first following on the disappearance of the colour of the bromine. The solution was vigorously shaken after each addition of hydrocarbon, and rapidly mechanically stirred, with external cooling, during the running in of the bromine solution. After neutralisation, the solution was distilled in portions through an efficient column in order to remove the bulk of the alcohol, and the product was removed from the residual liquid by extraction with ether, and directly reduced by means of an excess of 3% sodium amalgam in dilute acetic acid at the ordinary temperature (hydrogen and palladised asbestos were also used), until, on working up a test portion, bromine was shown to be absent. The unsaturated alcohols were extracted from the neutralised solution by means of ether, dried with potassium carbonate, and esterified by warming on the water-bath for 20 hours with twice their weight of acetic anhydride. The esters, b. p. 120—140°, which were isolated by extraction with ether after hydrolysis of the excess of acetic anhydride, were shown by analysis and quantitative saponification to consist essentially of acetoxypentenes, containing, in all probability, a certain amount of ethoxypentenes arising from the direct intervention of alcohol in the original reaction with bromine. The yields throughout were excellent.

The ozonides obtained from the acetoxypentenes by treatment with ozonised oxygen in methylene chloride below — 30° were freed as much as possible from this solvent by passage of a stream of dry oxygen under reduced pressure at 0°, dissolved in ether, and reduced with successive small portions of aluminium amalgam until the reactions of ozonides were no longer obtained. The filtered ethereal solution was distilled up to 36° through a long Dufton column into a small amount of ice-water and the ethereal layer in the distillate-receiver was re-extracted with water. The combined aqueous solutions responded to tests for formaldehyde and acetaldehyde; the *p*-nitrophenylhydrazone which was isolated proved to be that of the former (m. p. and mixed m. p.). The qualitative recognition of acetaldehyde was based on (*a*) the formation of a white precipitate with Leys's reagent (a solution of yellow mercuric oxide in alkaline aqueous sodium sulphite), and (*b*) the development of a blue colour with sodium nitroprusside and piperidine. When the residue from the distillation of the ether and its more volatile solutes was distilled, the first runnings, b. p. 36—65°, were found to be rich in acetone, the *p*-nitrophenylhydrazone and 2 : 4-dinitrophenylhydrazone of which were isolated (m. p.'s and mixed m. p.'s) : in one experiment the yield of the latter represented approximately 40% of the original acetoxypentenes. The treatment of the remaining fraction, b. p.

50—80°/19—15 mm., became modified as our knowledge of its behaviour increased. In the earlier experiments it was partly separated into less and more volatile fractions, which were hydrolysed as described below, and it was in this way that the main constituents of the mixture were originally recognised. With the quantities at our disposal, however, separation by distillation was unsatisfactory, and, in the later experiments, the whole fraction was hydrolysed by warming it for a short time with very dilute sulphuric acid. Ether was added, the sulphuric acid precipitated with freshly prepared barium carbonate, the aqueous solution extracted twice with ether, and the ethereal solution washed once with water, dried, and distilled. α-Hydroxy*iso*butaldehyde was thus obtained, in yields up to 16 mols. % of the acetoxyaldehydes, as a liquid, b. p. 134—136°, which subsequently crystallised, the solid having m. p. 64—66° (Found: C, 54·1; H, 9·4. Calc.: C, 54·5; H, 9·1%). The combined aqueous extracts contained glycollaldehyde, which, having been qualitatively recognised, was roughly estimated by means of Fehling's solution (reduction occurs in the cold), and then precipitated in the form of its phenylosazone, m. p. 169° (Found: C, 70·5; H, 5·9; N, 23·7. Calc.: C, 70·6; H, 5·9; N, 23·5%). For the preparation of the osazone a standard procedure, based on that of Fenton and Jackson (J., 1899, **75**, 578), was used which was known to lead to a 60% conversion. The reduction of copper salts indicated a content of the aldehyde corresponding to 51%, and the yield of osazone, on the basis of the conversion given, represented glycollaldehyde equivalent to 47% of the original acetoxyaldehydes.

Action of Bromine and Water on α-Phenylbutadiene.—Muskat and Grindley (*J. Amer. Chem. Soc.*, 1930, **52**, 1574) have examined the action of halogen-free hypochlorous and hypobromous acids on α-phenylbutadiene; their oily addition products yielded much benzaldehyde on ozonolysis and that derived from hypochlorous acid gave δ-chloro-α-phenylbutadiene amongst the products of its thermal decomposition.

The hydrocarbon, prepared from cinnamaldehyde and methylmagnesium bromide by Heide's method (*Ber.*, 1904, **37**, 2103), had b. p. 90—91°/15—16 mm., and it crystallised on cooling in ice. The methods of treatment with bromine and of reduction of the product were substantially the same as those described in relation to the experiments on isoprene. The halogen-free material on distillation gave a more volatile fraction, probably containing γ-phenyl-α-methylallyl ethyl ether, together with a main fraction, b. p. 133—135°/14—15 mm., consisting of γ-phenyl-α-methylallyl alcohol (Found: C, 80·8; H, 8·0. Calc.: C, 81·1; H, 8·1%), which was identified by the m. p. (93°) of its phenylurethane, and the mixed m. p. of this compound with a specimen derived from a sample of alcohol prepared according to Klages's method (*Ber.*, 1902, **35**, 2650). The ozonide of the more volatile fraction on boiling with acidified water gave benzoic and pyruvic acids, of which the latter was identified by the preparation of its phenylhydrazone (compare Burton, J., 1929, 455).

Action of Bromine on α-Bromobutadiene.—The bromohydrocarbon, prepared from pure butadiene dibromide (m. p. 54°) by Willstätter and Bruce's method (*Ber.*, 1907, **40**, 3924), had b. p. 91—93°. Treatment with bromine (1 mol.) (*a*) in hexane at — 35°, (*b*) in chloroform at — 35°, (*c*) in chloroform at + 35°, and (*d*) in acetic acid at 20°, followed by direct distillation of the solvent and subsequently of the product, yielded in all cases a straw-coloured oil, b. p. 110—112°/15 mm., 114—115°/18 mm., 109—112°/14 mm., 115—116°/20 mm., which was identified as *αγδ-tribromo-Δ^{α}-butene* (Found: C, 16·5, 16·8, 16·7, 16·7; H, 2·1, 1·8, 2·0, 1·9; Br, 81·6, 82·1. $C_4H_5Br_3$ requires C, 16·4; H, 1·7; Br, 81·9%). All four specimens on ozonolysis by the second or third of the methods described in connexion with the degradation of the chlorodibromobutenes yielded carbon monoxide, hydrogen bromide, and, α-bromoacraldehyde (Found: C, 26·7, 26·6; H, 2·3, 2·3%; semicarbazone, m. p. and mixed m. p.'s, 160°).

Action of Hydrogen Bromide on α-Bromobutadiene.—Dry hydrogen bromide (1 mol.), free from bromine, was liquefied and subsequently allowed to set to a compact solid mass in a tube cooled in liquid air. Dry ether was added and after this had solidified above the hydrogen bromide the bromohydrocarbon was introduced, and the tube was sealed, kept at the ordinary temperature for several days, and finally heated at 60° for 1 hour. No great pressure was released when the tube was opened, and the product, after removal of the ether, had b. p. 59—61°/15 mm., and gave no indication of containing a more volatile fraction (Found: C, 22·1; H, 2·7; Br, 75·0. $C_4H_6Br_2$ requires C, 22·4; H, 2·8; Br, 74·8%). The substance was identified as *αγ-dibromo-Δ^{α}-butene* by its behaviour towards permanganate. When it was treated with this reagent (equivalent to 4·5 atoms of oxygen) in aqueous acetone in the presence of excess of magnesium sulphate, first at the ordinary temperature and later at 35—40°, a product was obtained which, on removal of the metallic oxides and the acetone, and working up for organic acids by thorough extraction of the acidified solution with ether, yielded only α-bromopropionic acid, b. p. 109—112°/14—15 mm., m. p. 22—23° (after one distillation). Owing to the hygroscopic character of this acid, its identification was completed by converting it into its chloride with thionyl chloride, and thence into the amide with ammonia in dry benzene.

Crystallised from benzene, the amide had m. p. 122—123°, both alone and after admixture with a specimen prepared from propionic acid *via* α-bromopropionyl bromide.

THE UNIVERSITY OF LEEDS.
UNIVERSITY COLLEGE, LONDON.

[*Received, September 9th,* 1931.]